LVII.—*Solution and Pseudo-solution. Part III. The Electrical Convection of certain Dissolved Substances.*

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Solutions of a Single Substance.

SOME preliminary experiments have already been described in the Trans. (1892, 61, p. 114), and although the work was unavoidably interrupted, we are now able to continue it; as, however, its completion must take a long time, we have thought it best, before entering on a new section, to publish the results we have obtained up to the present time.

It may be well briefly to recall that our work began with some qualitative observations on the conductivity of arsenious sulphide solution, the various "grades" of which have been described in previous parts (Trans., 1892, 61, 148, and 1895, 67, 63).

The resistance of such a solution is extremely high, and the current passing through it amounted in one case to only 0.000007 ampere. The conductivity is probably due to the presence of small traces of arsenious oxide; but, however that may be, the passage of this small amount of current is accompanied by the repulsion of the colloidal sulphide as a whole from the negative electrode. An examination of this repulsion of the dissolved substance has now been made with a variety of suitable solutions, but at present we have chiefly examined coloured solutions, as observations with them are obviously the easiest. These include, however, various grades of solution. Some of the solutions examined (such as arsenious sulphide (γ)*, and colloidal ferric hydrate), were too coarse-grained to pass through a porous pot, others (as aniline blue and iodine) were readily filterable, and did not contain particles large enough to scatter light. With the colloidal solutions which reveal a coarse grained structure by the optical test (Tyndall's experiment), we have (*e.g.*, arsenious sulphide, ferric hydrate, and silicic acid) found it impossible to repel the dissolved substances vertically upwards as completely as downwards. If *A* is the cathode in the arrangement shown, the colloid is readily repelled downwards. If now, when it has been driven some distance, we reverse the current so that *B* becomes the cathode, the sharply-defined surface of the yellow sulphide begins to rise and the sulphide is driven upwards, but it is never repelled clear of the electrode *B*. Presumably, this is due to the action of gravity on the large colloidal particles. With a dilute higher grade solution, on the other hand, the dissolved substance can be repelled completely from the lower electrode. For instance, Magdala red, aniline blue, &c., can be repelled in this way. Usually, when a strong solution of such dyes is employed, it has not been found possible to secure complete repulsion, however the electrodes are placed, but only a difference of concentration at the two electrodes. With aniline blue, however, complete repulsion can be obtained, even with strong solutions (2 or 3 per cent.).

It is noticeable that, when compounds are dissolved in a very perfectly non-conducting medium, such as carbon bisulphide, no repulsion is observed. Thus iodine in solution in a not perfectly non-conducting medium is repelled from the negative electrode, whilst, in carbon bisulphide, which offers enormous resistance, no repulsion could be observed with an E.M.F. up to 210 volts. Similar results were obtained with "methyl-violet," which is repelled from the anode. When extremely small currents are concerned, the repulsion seems to vary with the strength of the current. Thus, using a mixture of

* Another grade of arsenious sulphide (δ) will pass through a porous pot, and is the highest grade solution of this sulphide obtained by us. It still scatters light.

carbon bisulphide, amyl alcohol, and ethylic alcohol as a solvent, the repulsion of iodine was much slower (the resistance being higher) than when (other conditions remaining the same) the solvent was ethylic alcohol. It remains to be seen whether the whole of the observed current is due to electrolysis, and how far, if at all, the non-electrolysed molecules take part in its conveyance.

The direction of repulsion has hitherto proved to depend on the chemical character of the dissolved substance; this will be seen on reference to the table, in which the results of a number of observations are collected. Thus, basic ferric hydrate is repelled from the positive electrode, whilst acidic arsenious sulphide is repelled from the negative electrode; the element iodine also is similarly repelled from the negative electrode. With the dyes mentioned as convenient for observation, the case is not so simple; aniline blue, whether as disodium salt or as sulphonic acid, was repelled from the negative electrode; there is considerable ground for considering many dyes as hydrolysed in solution. Considering the disodium salt of aniline blue as hydrolysed, we have in solution sodium hydroxide and the sulphonic acid.* The repulsion from the negative electrode is, then, a repulsion of the sulphonic acid. On this hypothesis, the same result should be obtained when the free sulphonic acid is used, and this proves to be the case.

Methyl violet is a hydrochloride. If we assume its hydrolysis into free acid and base,† repulsion, according to chemical character, would mean repulsion from the positive electrode; this is the observed repulsion.

Magdala red, also, on hydrolysis, would yield base and hydrochloric acid, and Hofmann's violet would yield the free base; it will be seen in the table that both these substances are repelled from the anode.

It is obviously impossible to classify some of the substances examined as basic or acid. In these cases, we must await further results for any generalisation that can aid us.

In certain cases, a slight, secondary repulsion has been observed in a direction opposite to that of the normal repulsion. Thus, after prolonged action of the current, a slight repulsion of arsenious sulphide from the anode is observed; this is also the case with ferric hydrate and with hæmoglobin.

It is noteworthy that the secondary repulsion only commences when

* In the case of the aniline blue disodium salt, the solution is blue, and that of the free acid is also blue; on adding sodium hydroxide to a dilute solution of the acid, it turns greenish and on further dilution again becomes blue.

† When used as a dye, it is the base which is taken up by the dyed substance. The whole of the hydrochloric acid remains in the bath (E. Knecht, *Ber.*, 1888, **21**, 1556). Methyl violet also shows colour changes on adding acid and diluting, which suggest hydrolysis.

‡ The account of the experiments with hæmoglobin will be found described in Part I. (*Trans.*, 1892, **61**, 148).

Substance.	Solvent.	Remarks.	R.
Aniline Blue (1)	Water	Filterable, diffusible, no beam	-
" "	Abs. alcohol	Non-filterable, beam	-
" " (2)	Water	Non-filterable, non-diffusible, beam.	-
" "	Abs. alcohol	Filterable, no beam	-
" " (3)	Water	Filterable, diffusible, no beam	-
" "	Alcohol	Filterable	-
Arsenious Sulphide γ (4)	Water	Non-filterable, diffusible, beam.	-
" " δ (4)	Water	Filterable, beam	-
Bromine	Alcohol	Filterable, diffusible, no beam	-
Ferric Hydrate (α)	Water	Non-filterable, non-diffusible, beam.	+
" " (β)	Water	Diffusible, beam	+
Hæmoglobin (Oxy) (5)	Water	Non-filterable, beam	+
" (CO) (5)	Water	Non-filterable, beam	+
Hofmann's Violet	Water	Not filterable,* diffusible, no beam.	+
" "	Alcohol	Filterable, no beam	+
" "	CS ₂	No beam	No R.
Indigo	Water	Beam	-
" "	Naphtha	"	No R.
Iodine	CS ₂	"	No R.
" "	Benzol	"	No R.
" "	Chloroform	"	No R.
" "	CS ₂ , C ₆ H ₁₂ O, C ₆ H ₆ O ..	"	-
" "	Alcohol	"	-
" "	Water, trace KI	Filterable	-
Magdala Red	Water	Non-filterable, very slow diffusion, beam.	+
" "	Alcohol	Filterable, non-polarised beam.	+
Methyl Violet	Alcohol	Filterable, no beam	+
" "	CS ₂	No beam	No R.
" "	Water	Not filterable,* diffusible, no beam.	+
Rosaniline Hydrochloride	Alcohol	"	+
Shellac	Water	Beam	-
Silicic Acid (7)	Water	Non-filterable, beam	-
Silver Hydrate	Water	"	+
Starch	Water	Non-diffusible, beam	-
Sulphur (α) (6)	Water	Beam	-
" (β)	Water	Beam	-
" (γ)	Water	Beam	-

(1) Disodium salt. (2) Sulphonic acid. (3) Monosodium salt. (4) Slight repulsion from + ve. (5) Some repulsion also from - ve. (6) (α) H₂S and SO₂; (β) Na₂S₂O₃ and HCl; (γ) S₂Cl₂ and water. (7) Five c.c. of liquid from cathode gave 6 milligrams residue, whilst five c.c. from the anode gave 72 milligrams residue.

* These colouring matters dye the substance of the pots used, and are thus withdrawn from aqueous solution.

Note.—In the above table, "filterable" means filterable through a porous pot; "beam" indicates that the substance scatters light showing a polarised beam. In the last column, - signifies repulsion from the negative electrode.

the first repulsion has almost attained its maximum effect. Suggestions as to the cause of this phenomenon could be made, but their only value is as a working hypotheses for directing further experiments.

Mixtures of Solutions.

In connection with the above, we have tried the effect of mixing together solutions of substances repelled from opposite electrodes. In general, we find that there is a tendency to aggregation between such substances. This may result either in complete coagulation, or simply in the formation of a more coarse grained solution. On mixing strong aqueous solutions of acidic and basic dyes, it is well known that a precipitate is formed,* and on mixing dilute solutions, the mixture shows a coarse grained structure (using the scattered light test), although neither of its constituents did so separately. The aggregates have formed a lower grade solution; the constituents of these aggregates being no longer free to move separately, can only be carried as wholes in the convection experiments. Aniline blue (-) is much more readily repelled than methyl violet (+) and, consequently, unless a large excess of methyl violet is used, the aggregates of the two dyes are repelled from the negative electrode. In presence of a large excess of methyl violet, these aggregates exhibit positive repulsion. The repulsion of silicic acid was first observed by dyeing the colloid molecules with methyl violet. The methyl violet was then carried with the acid from the cathode, its normal repulsion being from the anode.

If now we could separate the constituents so as to cause what we may venture to call dissociation of the aggregates, the separated dyes should once more exhibit their individual repulsion; this result can actually be obtained by the addition of alcohol. On now passing the current through the solution, the dyes are repelled in opposite directions, and the aniline blue concentrates at the anode, whilst the methyl violet concentrates at the cathode.

Similar results can be obtained with aniline blue and Magdala red. An aqueous solution of the latter is obtainable by adding some concentrated alcoholic solution to water, a low grade solution being formed; on mixing this with aqueous aniline blue in strong solution, coagulation occurs, but, in dilute solutions, coagulation does not occur. The optical test is not available in this case for detecting aggregation, as the Magdala red particles already scatter and polarise light; we can, however, utilise the fact that aniline blue, when present singly in aqueous solution, is filterable through a porous pot. After mixing the

* The dyes do not merely combine as wholes. The mechanism of these reactions is being examined by us as part of an investigation of the coagulation of low grade solutions.

aniline blue and Magdala red, neither of the constituents will pass through a porous pot. As in the last case, if the aggregates are dissolved by alcohol, their dissociation is shown by the separate repulsion of their individual constituents.

Similar results are obtainable with rosaniline hydrochloride, and aniline blue. In like manner, the compound of methyl violet with silicic acid, mentioned above, is dissociated by alcohol, or, to put it in another way, the dye is dissolved out of the colloid molecules, and can then exhibit its individual repulsion.

It will be at once apparent that we have here a remarkable mimicry of ionic dissociation. The question presents itself, are these slowly moving molecules conveying the current in a way at all analogous to conduction by ions? Colloids are stated not to conduct, but we are making an attempt to solve this problem with some of our higher grade colloid solutions. One interesting observation should be noted; we have from time to time observed a banded structure during some of these separations, reminding one of the stratification observed with mixtures of highly-rarefied gases. The exact conditions necessary to produce this effect have not yet been ascertained.

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