violet effects are, of course, possible, and the mechanism suggested can only be considered as a working hypothesis. Experiments are in progress in this laboratory to test the point.

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Electromigration of Iodobismuthite in Colloidal Systems.

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Electromigration of the complex ion (BiI_5) of sodium iodobismuthite (Na_2BiI_5) in colloidal systems is of interest in connection with the absorption and cerebrospinal penetration of this electronegative bismuth in antisyphilitic medication.[1] The red (BiI_5) ion migrates to the anode in aqueous, alcoholic and glycolic media.[2] The question of cerebral and spinal fluid penetration hinges, partly at least, on another question, whether the unchanged complex ion (BiI_5) can migrate in colloidal systems analogous to those of the body, such as serum and a gel. Direct test of migratibility in living tissue and blood is practically impossible. Therefore, a special electrolytic cell, which also acted as a model, containing serum, agar-gel, and iodobismuthite was used.

The anionic character of the bismuth in iodobismuthite was originally demonstrated with bare platinum electrodes.[2] However, such electrodes require constant attention in order to avoid decomposition of the labile complex (BiI_5) ion. Therefore, the use of KCl-agar bridges in the anode and cathode chambers was suggested, since their use would prevent loss of the electrical charge on, and consequent decomposition of, the complex (BiI_5) ion. This arrangement also made it practically feasible to test the migration, if any, of the (BiI_5) ion in colloidal systems, *i. e.*, into serum and from serum into the agar-gel. The analogy to conditions prevailing in the intramuscular administration of iodobismuthite (iodobismitol) was al-

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1 Hanzlik, Mehrtens, Gurchot and Johnson, *J. Am. Med. Assn.*, 1932, **98**, 537; Hanzlik and Spaulding, *Am. J. Syph.*, 1932, **16**, 335; Hanzlik, Mehrtens and Spaulding, *Am. J. Syph.*, 1932, **16**, 350.

2 Hanzlik and Spaulding, PROC. SOC. EXP. BIOL. AND MED., 1931, **28**, 847; Gurchot, Hanzlik and Spaulding, *J. Pharm. Exp. Therap.*, 1931, **45**, 427.

most perfect. That is, in the model, the serum phase corresponded to the lymph and plasma (blood) with which iodobismuthite comes in contact when injected intramuscularly, and the agar-gel phase, to the tissues and brain to be penetrated. Such an electrical field does not exist, of course, in the living fluids and tissues. The chief importance of this test is the demonstration of the possible migration and survival of the complex (BiI_5) ion in aqueous colloidal systems without hydrolysis, or at least with retarded hydrolysis.

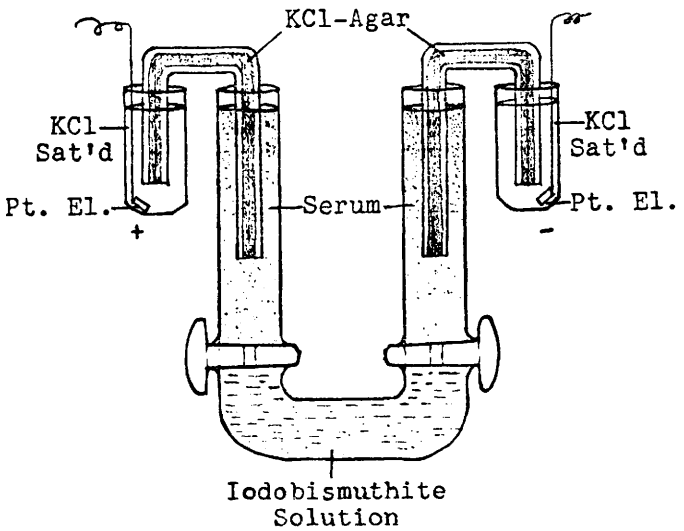

FIG. 1.
Diagram of arrangement for electromigration of iodobismitol in colloidal systems.

As the electrolytic cell used may be of general interest, and its application appears to be novel, a short description and a diagram are presented. The parts of the cell are sufficiently evident from the diagram in Fig. 1. We commonly use Pyrex glass tubing of 8 mm. bore for the U-tube and suitable stop-cocks, height over all being 12 cm., and the part under the stop-cocks, about 2 cm. The tubes holding the saturated KCl solution and the platinum electrodes are ordinary small test tubes, 70x14 mm. The glass tubes for the KCl-agar bridges are of 3 mm. bore, total length 22 cm. The agar-gel is saturated with KCl in the usual manner. The cell is operated as follows: The U-part beneath the stopcocks is filled with the solution to be migrated to the upper level of the stop-cocks, which are then closed; any solution in the chambers above is washed out and the serum, or other medium, is run in to the same level in both chambers. The KCl-agar bridges, connected with the saturated KCl

solution, are now inserted into the chambers to equal positions about 4 cm. above the stop-cocks, which are then carefully opened, and a current of 110 v. is turned on.

When the ion is colored, as in the case of iodobismuthite, the boundary is seen to move toward the anode and correspondingly away from the cathode in less than 1 hour. A standard time of 1 or 2 hours, with this cell, will suffice for many experiments; in other cases, 24 hours or longer may be necessary or desirable. By the end of 8 to 24 hours, the boundary may have reached the KCl-agar bridge. In qualitative experiments, the presence of an ion in the chamber fluids and in the agar, such as bismuth, may be simply identified by the color or by adding hydrogen sulphide test solution, or by both these tests. In quantitative experiments, the chamber fluids and the bridge-agars are analyzed separately.

The principal variables affecting the electromigration are: fluctuations in electric current which affect the time; electrolyte concentration of the fluid to be migrated and of the chamber-fluids which affect the speed, the higher the concentration the greater the speed; diffusion from the boundaries which affects the ion-content of the chamber-fluids, this being negligible in short experiments but must be deducted from the total ion-content of each chamber in long experiments, such as 24 hours or more; physical disturbances in the ordinary laboratory which tend to vitiate results with the cell. The agar is, of course, not affected by diffusion or physical disturbances, and therefore, the use of KCl-agar bridges is a decided advantage. An even greater advantage of the agar-bridges over bare platinum electrodes is that the decomposition voltage of any compound can be neglected.

In actual experiments with sodium iodobismuthite, the following results were obtained: Using 6% sodium iodobismuthite in ethylene glycol, boundary movement of the red fluid (BiI_5 ion) toward the anode occurred in about 1 hour, more definitely in 2 hours, and reddish-yellow staining of the KCl-agar anode in 5 to 6 hours; presence of bismuth being confirmed by positive tests with H_2S. In 24 hours, the KCl-agar anode was deep yellow to brownish and, since tests for free iodine were negative, the coloring was due to the (BiI_5) ion. On the other hand, the boundary moved away from the cathode, the chamber-fluid remained colorless and the KCl-agar cathode was not stained and tests with H_2S were negative. Similar results were obtained with iodobismitol (12% NaI, and 6% Na_2BiI_5 in ethylene glycol). Thus the results confirmed the original claims for the electronegativity of Bi in iodobismuthite. The same

qualitative results were obtained for ethylene glycol, glycol acidified with acetic acid, 25% acetic in water, alcohol acidified with acetic acid, 95% alcohol, and horse serum in the chambers.

Quantitative results in 15 experiments with natural and dialyzed serums in the chambers, and 6% iodobismuthite in glycol, were as follows: Runs of from 3 to 24 hours, median 24 hours, gave 0.04 mg. Bi, median (range, 0.002 to 0.43 mg.) in the KCl-agar anode and 0.001 mg. Bi, median (range, 0 to 0.02 mg.), the median difference in favor of anionic Bi being 0.031 mg., or a concentration of 1:64,000 in the agar-gel. There were 2 gm. of KCl-agar gel in each bridge. The serum of the anode chamber showed 0.17 mg. Bi, median (range, 0.03 to 0.4 mg.), and of the cathode chamber, 0.02 mg. Bi, median (range, trace to 0.6 mg.), the median difference in favor of anionic Bi being 0.13 mg. or a concentration of about 1:100,000 in the serum. No deduction for diffusion was necessary from the Bi of the KCl-agar electrodes, but from the chamber-fluids quantities of 0.003 mg. (median) were deducted, according to results of 24-hour runs in 12 experiments of the same kind except for passage of the electric current. In the short runs, as in the qualitative experiments, the results were unaffected by diffusion, but, in long runs, some hydrolysis of the (BiI_5) ion apparently occurred. Nevertheless, the preponderant migration of the iodobismuthite in the vast majority of experiments was as the electronegative (BiI_5) ion in both serum and agar-gel. The bismuth in these experiments was estimated according to a method previously described.[3]

Conclusions. A simple electrolytic cell which guards against decomposition of labile, complex ions, which is also suited to tests of electromigration in colloidal systems and tends to overcome objections to the use of bare platinum electrodes in ordinary cells, is described. Electronegative migration of the colored iodobismuthite (BiI_5) ion is demonstrable in different solvents, and in colloidal systems, such as serum and agar-gel, in confirmation of previous claims for electronegativity of this bismuth compound by other methods. The colloidal migration in the model used correlates with the results on absorption and cerebrospinal penetration of the iodobismuthite.

[3] Hanzlik, Mehrtens, *et al.*, *Arch. Derm. Syph.*, 1930, **22**, 483.