

## ELECTROLYSIS OF SODIUM IODOBISMUTHITE SOLUTIONS.\*

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Iodobismitol, a solution of sodium iodobismuthite and sodium iodide in ethylene glycol, has been shown by Hanzlik, Mehrten, Gurchot and Johnson (1) to be of value in the treatment of syphilis. Sodium iodobismuthite has the empirical formula— $\text{Na}_2\text{BiI}_5$ —and has been described by Nickles (2), Astre (3) and Draggendorf (4). Hanzlik has stated that the bismuth in this compound, more especially in Iodobismitol, is anionic, whereas most bismuth solutions contain cationic bismuth; the anionic character of the bismuth is reported as being related to the therapeutic efficacy of Iodobismitol. The present paper describes in detail a simple and rapid method by which the migration of the bismuth in Iodobismitol may be demonstrated; this method was suggested to us by Hanzlik.

## APPARATUS.

The cell is a "U" tube having legs 20 cm. long and 7 mm. internal diameter. A stop-cock is sealed into each leg 15 cm. from the top; this cock makes it possible to fill the bottom of the "U" and the cocks with the solution to be tested, close the cocks, clean the upper part of each leg completely (this is essential) and fill the tubes above the cocks with any desired liquid so that there will be no traces of the test solution in the upper parts of the legs, *i. e.*, the electrode chambers, and so that the division between the test solution and the overlaying liquid will be sharp. When the cell has been filled, platinum screen electrodes which are connected to a 110 volt direct current are inserted into the liquids in the electrode chambers so that the bottom of each electrode is 7.5 cm. above the stop-cocks.

## PROCEDURE.

Iodobismitol is placed in that portion of the cell between the stop-cocks, filling the cocks. The electrode chambers (the legs above the stop-cocks), after completely removing any traces of the Iodobismitol solution, are filled with 75% aqueous acetic acid. The electrodes are inserted, the current is turned on and the stop-cocks are carefully opened.

## OBSERVATIONS.

1. *Current.*—At the outset the current flow is 0.21 m. a. but it gradually rises to 0.62 m. a. at the end of three hours.

2. *Migration.*—(a) Shortly after the current has been turned on the red Iodobismitol solution moves toward the anode and can be seen above the top of the stop-cock, whereas the level of the red Iodobismitol does not change on the cathode side.

(b) After two hours the red color has risen 2.7 cm. above the stop-cock on the anode side and a noticeable amount of iodine is liberated at the anode. No change is detectable in the liquids on the cathode side with the exception of a dark stain (bismuth) on the cathode.

(c) After three hours the amount of iodine liberated at the anode has become so great that the migration of the red Iodobismitol solution toward the anode is obscured.

3. *Chemical Tests Demonstrating Migration.*—The stop-cocks are closed and the current is shut off. The liquid surrounding the anode gives a positive test for bismuth and for free iodine. The black stain on the cathode is removable with aqua regia and the residue obtained by evaporating the aqua regia gives a positive test for bismuth.

The foregoing is the simplest and most rapid method for demonstrating the migration of bismuth during the electrolysis of Iodobismitol. The chief difficulty

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with the method is the tendency of the liberated iodine to obscure the extent of migration of the colored solution toward the anode. This has been successfully avoided by using a different type of cell and different conditions as described below:

#### APPARATUS.

This cell (diagram 2) is specially designed to permit removal separately of the overlayering liquids in the electrode chambers, withdrawal of the iodobismuthite solution or addition of material (acid or sodium iodide) to the overlayering liquids or the iodobismuthite solution without disturbing the rest of the experiment. Also, the electrodes are so placed in special side arms as to prevent any material, such as iodine, liberated at the anode, from diffusing back and obscuring the phenomena to be observed during the electrolysis.

#### PROCEDURE.

A 1% solution of sodium iodobismuthite in ethylene glycol is placed in the "U" shaped portion of the tube between the stop-cocks. It is overlayered with a 0.2% sodium iodide solution in ethylene glycol 3 parts—water 1 part; the space

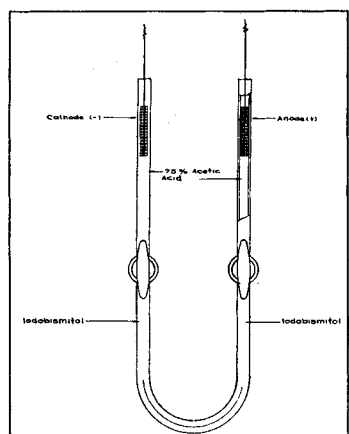


Fig. 1.

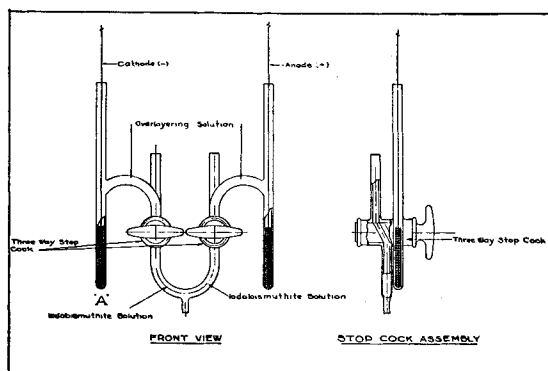


Fig. 2.

(A) surrounding the cathode is filled with  $N/5$  hydriodic acid in ethylene glycol. After twenty-four hours' electrolysis the current has risen to a maximum of 0.12 m. a. and remains at this level. The cathode has a black stain on it as usual and the interface between the iodobismuthite solution and the liquid surrounding the cathode has dropped 2.5 cm. while the colored solution has migrated 3 cm. toward the anode which is surrounded by a brown color of free iodine. At this point the stop-cocks are closed and the solutions surrounding the anode and cathode are withdrawn. Fresh solutions are then substituted for them and the iodobismuthite solution remaining between the cocks is treated with sodium iodide equal to three-quarters of the amount originally present and thoroughly mixed. The current is again turned on. During the second twenty-four hours the current reaches a maximum of 0.4 m. a. and at the end of this period there is a depression of the interface between the iodobismuthite solution and the solution surrounding the cathode of 3.75 cm. Again there is migration of color toward the anode with much liberation of iodine at the anode. The solutions surrounding the electrodes are again

removed and replaced with fresh solutions and again the sodium iodide, 30 mg., is put into the iodobismuthite solution. The current is again turned on and the maximum during the third twenty-four hours is 0.4 m. a. At the end of the third twenty-four-hour period the appearance of the experiment is much the same as at the end of the second twenty-four hours. The electrolysis is allowed to proceed undisturbed for four more days, making a total of seven days. At the end of this period the current has fallen to zero, the interface between the iodobismuthite solution and the liquid surrounding the cathode is 2.5 cm. below the stop-cock and there is a noticeable black stain on the cathode. The anode is surrounded by a brown iodine solution and the colored iodobismuthite solution has migrated toward the anode to a large extent. The iodobismuthite solution remaining between the stop-cocks is extremely pale showing that most of the bismuth has been removed by electrolysis.

## ASSAYS.

Bismuth in original iodobismuthite solution		5.9 mg.
Bismuth in anode liquid:		
(a) 1st stage	2.1 mg.	
(b) 2nd stage	1.6 mg.	
(c) 3rd stage	0.8 mg.	
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Total	4.5 mg.	
Bismuth on cathode	0.4 mg.	
Unmigrated bismuth	1.5 mg.	
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Total recovered		6.4 mg. <sup>1</sup>

<sup>1</sup> This figure, the sum of 5 separate assays, is 0.5 mg. above what it should be, due no doubt to limits of accuracy in the separate assays.

This procedure shows that most of the bismuth in the solution will migrate toward the anode if fresh electrolyte, sodium iodide, is periodically added. In this procedure anodic migration is not obscured by the presence of free iodine diffusing back into the iodobismuthite solution.

## REFERENCES.

- (1) Hanzlik, Mehrtens, Gurchot and Johnson, *J. Am. Med. Assoc.*, 98 (1932), 537.
- (2) Nickles, *J. pharm. chim.* (3), 40 (1861), 324; (3), 41 (1862), 148; *Compt. rend.*, 50 (1860), 872.
- (3) Astre, *Compt. rend.*, 110 (1890), 525, 1137.
- (4) Draggendorf, *Pharm. Ztg. Russia*, 5 (1866), 82.

RESEARCH DEPT. OF THE CHEMICAL & PHARMACEUTICAL LABORATORIES,  
E. R. SQUIBB & SONS,  
BROOKLYN, N. Y.

*A. Ph. A. Resolution No. 3. Dispensing of Liquor for Medicinal Purposes.*

*Resolved*, that the Officers and Council of the AMERICAN PHARMACEUTICAL ASSOCIATION be instructed to take such steps as they may deem necessary in the event of repeal of the 18th amendment, to prevent the sale of beverage liquor in pharmacies or drug stores, and be it further

*Resolved*, that it shall be the declared policy of the AMERICAN PHARMACEUTICAL ASSOCIATION to favor the dispensing of liquor for medicinal purposes only on physicians' prescriptions.