IMMERSION LIQUIDS OF HIGH REFRACTIVE INDEX*

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ABSTRACT

A new series of high-index immersion liquids (1.74 to 2.00) has been made. Methylene iodide and a solution of precipitated sulfur (10 per cent) in arsenic tribromide are the end members of the liquids between 1.74 and 1.81. The mixing curve is not a straight line. The end members of the liquids from 1.82 to 2.00 are a solution of precipitated sulfur (10 per cent) in arsenic tribromide, and a solution of precipitated sulfur (20 per cent) and arsenic disulfide in arsenic tribromide (60 per cent). This mixing curve is a straight line.

The temperature coefficient of the liquids is of the same order of magnitude as that of methylene iodide but the dispersion is higher. After six months the maximum change in index of the liquids between 1.74 and 1.81 was ± 0.001. For the liquids between 1.82 and 2.00 it was ± 0.003.

Liquids of various combinations have been made from arsenic tribromide, arsenic disulfide, arsenic trisulfide, sulfur, selenium, mercuric sulfide, antimony bromide, and α-bromonaphthalene. The highest index obtained was 2.1 for a mixture of arsenic tribromide, arsenic disulfide, and selenium.

INTRODUCTION

A study of inorganic, organic, and metal-organic compounds that might be employed in the preparation of high refractive index liquids is in progress at the U. S. Geological Survey. It is part of a program of research in the geochemistry of uranium which the Survey is undertaking on behalf of the Atomic Energy Commission.

As part of this study, a new series of immersion liquids that range in index from 1.74 to 2.00 has been made. The 1.74 to 1.81 liquids contain methylene iodide, precipitated sulfur, and arsenic tribromide. Those from 1.82 to 2.00 contain arsenic tribromide, precipitated sulfur, and arsenic disulfide.

It is now six months since complete sets of these liquids were made and distributed for testing. The favorable comment of the mineralogists and petrologists who have used them, and the interest in them that others have shown, warrants their introduction for general use so early in their development.

The authors intend to present a complete report on this series of liquids after they have been in use for at least a year. Meanwhile, a brief description of the liquids, together with their limitations and the method that has been used for their preparation, are presented here. These liquids are a further development of the arsenic tribromide liquids described by L. H. Borgström (1929, 1933) of Finland.

The liquids containing methylene iodide, sulfur, and arsenic tribromide

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were originally yellow amber in color but darkened on standing because of the decomposition of methylene iodide. The liquids containing arsenic tribromide, sulfur, and arsenic disulfide range in color from yellow to dark amber.

A disadvantage inherent in all liquids containing arsenic tribromide is its acidic properties *per se* and the fact that it forms by hydrolysis with water or water vapor hydrobromic acid and a white precipitate of arsenic trioxide. Because of their acidic nature these liquids will react with some minerals. The corrosion of metals can be avoided by taking the proper precautions, and the effect of hydrolysis can be made negligible by making the immersion rapidly. The liquid when covered quickly by a coverslip will remain stable. These liquids must be stored in glass bottles with a ground-glass stopper and a ground-glass dust cover.

Some of the liquids have developed a slight turbidity. This turbidity is due to the presence of very fine grained crystals which are not objectionable in ordinary immersion work. The 1.98, 1.99, and 2.00 liquids were supersaturated with respect to sulfur when originally prepared. It takes some time for these high-index liquids to come to equilibrium. The sulfur that precipitates from solution will be in the form of realtively large crystals that can be removed easily by filtration through sintered glass. The liquid itself remains clear. The 1.80, 1.81, and 1.82 liquids may become solid if the temperature at which they are stored falls much below that of normal room temperature (20° to 25° C.). Gentle warming will effect complete solution and after thorough mixing the clear liquid will have its original refractive index.

After a period of six months the maximum change in index of the liquids between 1.74 and 1.81 was ± 0.001; for the liquids between 1.82 and 2.00 it was ± 0.003.

The temperature coefficient (dn/dT) of the liquids between 1.74 and 1.81 is 7×10^{-4}. That of the rest of the series is 6×10^{-4}. The dispersion, as measured by the differeace in index between the "e" line of mercury (546) and the "D" line of sodium (589), is as follows:

α-bromonaphthalene	76×10^{-4}
Methylene iodide	88×10^{-4}
1.74 liquid	96×10^{-4}
1.81 liquid	103×10^{-4}
1.83 liquid	116×10^{-4}
2.00 liquid	174×10^{-4}

Preparation of Immersion Liquids

Liquids between 1.74 and 1.81

Reagents.—1. Methylene iodide, Eastman Organic Chemical No. 167

supplied by Distillation Products Industries, Rochester 3, N. Y.

2. Sulfur, precipitated, U.S.P.

3. Arsenic tribromide, C.P., supplied by A. D. Mackay, Inc., 198 Broadway, New York 7, N. Y.

The end members are:

1. Methylene iodide, $n_{Na}^{25^\circ C.} = 1.738$

2. 10 per cent sulfur in arsenic tribromide, $n_{Na}^{25^\circ C.} = 1.814$

Preparation of solution of 10 per cent sulfur in arsenic tribromide.—The sulfur and arsenic tribromide (10:90 by weight) are mixed in a glass-stoppered Erlenmeyer flask and solution is effected by gentle warming. After standing at room temperature overnight, the solution is filtered by suction through a sintered glass of "medium" porosity. The filtrate is passed through the same filter until it is no longer turbid.

The mixing curve obtained with the two end members deviates considerably from a straight line, and the curve may be constructed from the following table.

10 per cent S in $AsBr_3$ (in grams)	Methylene iodide (in grams)	$n_{Na}^{25^\circ C.}$
5.4	174.6	1.742
21.6	158.4	1.753
36.9	143.1	1.762
52.2	127.8	1.771
71.1	108.9	1.781
92.7	87.3	1.792
119.7	60.3	1.801
158.4	21.6	1.811

The necessary amounts by weight of the high and low end members are mixed together in glass-stoppered bottles or Erlenmeyer flasks to obtain the series of liquids of desired intervals. The refractive indices of the liquids are determined after thorough mixing.

Liquids between 1.82 and 2.00

Reagents.—1. Sulfur, precipitated, U.S.P.

2. Arsenic tribromide, C.P.

3. Arsenic disulfide, C.P., supplied by A. D. Mackay, Inc., 198 Broadway, New York 7, N. Y.

The end members are:

1. 10 per cent sulfur in arsenic tribromide, $n_{Na}^{25^\circ C} = 1.814$

2. A solution of sulfur and arsenic disulfide in arsenic tribromide whose composition is 20:20:60 by weight, $n_{Na}^{25^\circ C} = 2.003$. These end members have a straight-line mixing curve.

Preparation of solution of sulfur and arsenic disulfide in arsenic tribromide.—To 60 parts by weight of arsenic tribromide in a glass-stoppered Erlenmeyer flask are added 20 parts by weight of sulfur. The mixture is warmed gently to effect solution. Then 20 parts by weight of powdered arsenic disulfide are added and the mixture is heated over a small flame, mixing constantly until a temperature of 100° C is reached. Heating is continued for 5 minutes, keeping the temperature of the mixture between 100° and 120° C. During the entire heating period the liquid is constantly mixed.

After standing at room temperature overnight, the solution is filtered by suction through sintered glass of "medium" porosity. The filtration will be very slow because of the high viscosity of the liquid. The filtrate may be slightly turbid.

The necessary amounts by weight of the high and low end members are mixed together in glass-stoppered bottles or Erlenmeyer flasks to obtain the series of liquids of desired intervals. The liquids are mixed thoroughly.

Each liquid is filtered by suction through sintered glass of "fine" porosity. The first portion of the filtrate may be slightly turbid. If so, the filtrate is passed through the same filter until it is clear. The refractive indices of the liquids are determined after thorough mixing.

The solutions or mixtures should be kept covered as much as possible during the preparation of all solutions containing arsenic tribromide because of the hydrolysis of arsenic tribromide by the water vapor in the air.

Liquids of various combinations have been made from arsenic tribromide, arsenic disulfide, arsenic trisulfide, sulfur, selenium, mercuric sulfide, antimony bromide, and α-bromonaphthalene. The highest index obtained was 2.1 for a mixture of arsenic tribromide, arsenic disulfide, and selenium.

The results of this study of compounds that might be used in the preparation of high refractive index liquids will be given in a series of reports, one of which will be a history and annotated bibliography of high-index immersion liquids and another a discussion of some theoretical aspects of liquids of high refractive index and the compounds they contain.

The cost of the materials used in the preparation of a set (1.74 to 2.00) of 27 immersion liquids, each containing 8 ml of liquid, is approximately $50. The price of the bottles to hold these liquids is about half this amount. This estimate is based on January 1950 prices of reagents and bottles which are as follows:

Arsenic tribromide, C.P.	$13.00 per lb.
Sulfur, precipitated, U.S.P.	0.55 per lb.

Methylene iodide, pure	4.50 per 100 g.
Arsenic disulfide, C.P.	13.33 per lb.
Bottles, dropping, with solid glass stopper drawn to a fine point for dropping, with glass cap ground on, 15-ml. capacity	0.65 each

References

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