IMMERSION MEDIA CONTAINING METHYLENE IODIDE

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ABSTRACT

The usefulness of methylene iodide as a constituent of immersion media is emphasized. The non-linear relationship of indices of refraction to composition by volume of some liquids containing methylene iodide is shown by experimental data.

An empirical equation has been devised for the calculation of indices of mixtures of methylene iodide and 1-bromonaphthalene from volume percentage data. Calculated indices show close agreement with experimental values.

The decomposition, purification, and preservation of methylene iodide is discussed.

Since 1886, when proposed by R. Brauns (1), methylene iodide, CH_2I_2, has been widely used as an immersion medium and as a constituent of immersion media prepared by mixing this substance with other liquids and solids. It is almost invariably used as a component of liquids whose indices of refraction are above 1.66 and has been recommended by Schroeder van der Kolk (2), F. E. Wright (3), Larsen and Berman (4), and others. Other organic derivatives (such as phenyldiiodoarsine (5), phenyl sulfide and mercury methyl (6)) have been proposed for the preparation of index liquids in upper ranges but the most popular material has probably been methylene iodide. Recently the usefulness of this compound has been emphasized by C. D. West (7) who has proposed a series of liquids composed of phosphorus, sulfur and methylene iodide to cover the range of indices from 1.74 to 2.06. According to Brunn and Barth (8), the stability of these media in storage leaves little to be desired.

Methylene iodide, despite its usefulness and popularity, has certain recognized disadvantages. It is expensive, is decomposed by light and heat, has relatively high dispersion and a larger temperature coefficient of refraction than liquids of lower refractive index. To the research worker who prepares his own liquids, perhaps the most annoying disadvantage of this substance is the departure of its mixtures from behavior as ideal solutions. It has been found that the properties of the commonly used mixtures of methylene iodide and other substances such as 1-bromonaphthalene are not straight-line functions of composition. This has been pointed out by Mayrhofer (9) in a recent paper on immersion liquids. Composition-refractive index data which have been gathered during the preparation of a series of immersion media containing methylene iodide are presented below.

Preparation of Liquids in the Range $n = 1.66$ to $n = 1.74$

The primary liquids used to prepare immersion media in this range were 1-bromonaphthalene and methylene iodide. Some workers have considered 1-chloronaphthalene as a desirable alternative for 1-bromonaphthalene but the author's work has shown that the employment of the latter can effect economy in the use of methylene iodide and reduce the total cost of a set of liquids. Further, impure 1-chloronaphthalene or "Halowax oil" is considered by Butler (10) to be undesirable for use in immersion liquids because it deposits gummy material which collects on the containers.

Buerger (11) has discussed the optical properties of ideal solutions and pointed out that the indices of refraction of liquids which form ideal solutions are linear functions of composition. However, Kaiser and Parrish (12) have presented data and mixing curves for methylene iodide and 1-chloronaphthalene proving that these liquids do not form ideal solutions. The data of Mayrhofer (9) and of the author show that methylene iodide and 1-bromonaphthalene also form solutions which are not ideal, and this is to be expected since the two naphthalene derivatives are quite similar.

Since mixtures containing methylene iodide have indices of refraction which are not linearly related to composition by volume, a simple formula for the composition of such liquids as presented by Schroeder van der Kolk (2), Buerger (11), or Rogers and Kerr (13) cannot be used for their preparation. However, the composition of such liquids may be calculated by means of an equation of higher degree as shown by Mayrhofer and Wratschko (14). In a recent paper in an obscure publication, these authors have presented an empirical equation which fits their experimental data with considerable accuracy. The equation is of the form:

$$y = A_0 + A_1x + A_2x^2 + \cdots + A_nx^n. \tag{1}$$

The empirical equation given is:

$$n_{20} = 1.658 + \frac{1}{10^7}(4000x + 43x^2) \tag{2}$$

in which x is the volume per cent of methylene iodide and n_{20} is the index of refraction of mixtures of 1-bromonaphthalene and methylene iodide in Na light at 20° C.

Re-evaluation of the empirical coefficients gives the following equation which shows better agreement with the author's experimental data:

$$n_{20} = 1.6587 + \frac{1}{10^7}(4530x + 37x^2). \tag{3}$$

Calculated values of n_D are given in Table 3 together with observed

experimental values. Differences between observed and calculated indices are of the same order as those found by Mayrhofer and Wratschko.

The calculation of percentage composition of liquids of desired indices using equation (3) is rather laborious. Therefore, a mixing curve or composition-refractive index curve prepared from experimental data will enable liquids of intermediate indices to be prepared quickly.

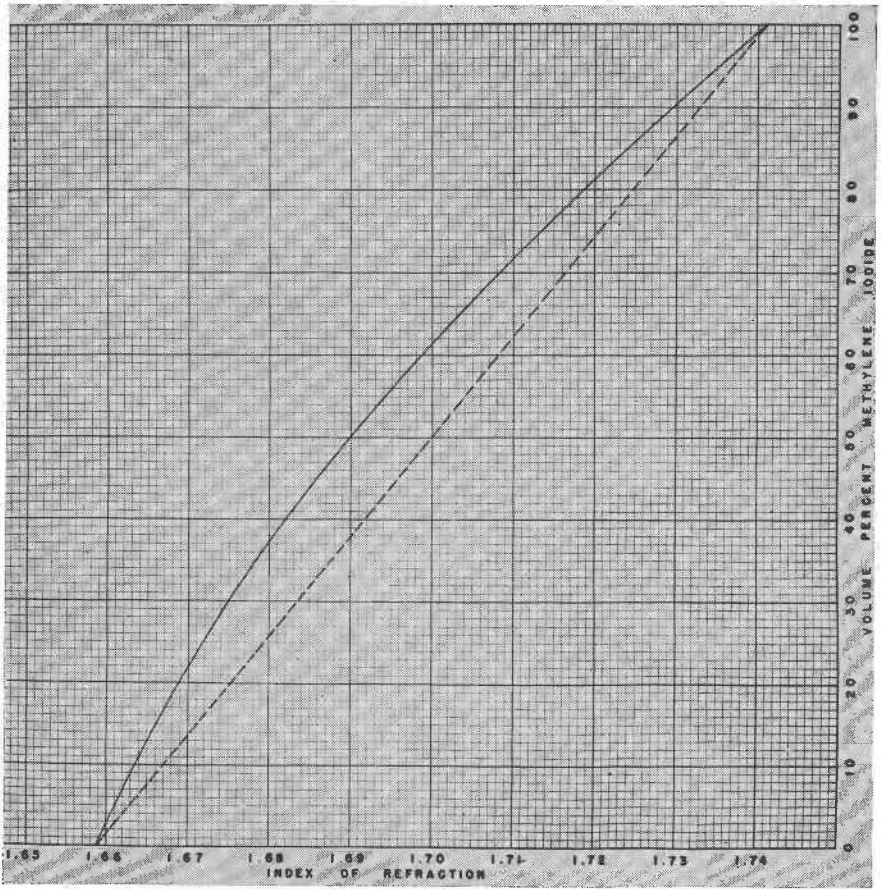

FIG. 1. Composition-refractive index curve for mixtures of methylene iodide and 1-bromo-naphthalene in Na light at 20° C. The solid curve is the graph of experimental data. The dashed straight line represents properties of a hypothetical ideal solution series.

Since some batches of chemicals used for the preparation of immersion media vary slightly in index of refraction, it is recommended that composition curves be prepared by each worker who undertakes the preparation of his own media.

The curves may be prepared easily by plotting composition against refractive index as shown in Fig. 1. A straight line representing the properties of ideal solutions may be drawn between points indicating the indices of the pure primary liquids. (Dashed line, Fig. 1.) Trial mixtures containing convenient volume percentages of the primary liquids should be prepared, thoroughly mixed, and the indices of refraction measured (Table 1). For purposes of comparison to determine the deviation of mixtures from ideal behavior, the volume percentages of trial liquids may be obtained from the straight line graph. When the indices are plotted against composition and a smooth curve drawn through these points and the values for the pure liquids, a curve results which is used to determine the composition of liquids with desired indices of refraction (Table 2). The accuracy of the method is determined by the accuracy of graphical interpretation and precautions taken in measuring the liquids.

The data for Fig. 1 which are tabulated in Tables 1 and 2 were obtained by using 10 ml. burettes which were graduated in 0.05 ml. Readings were estimated to 0.01 ml. Volumes of individual mixtures prepared were 10 ml. The liquids used were fresh stock chemicals obtained from the Eastman Kodak Company, Rochester, New York. The indices of refraction for Na light ($\lambda = 5893$ Å.) were measured on a one-circle goniometer by the method of minimum deviation, using a prism provided with circulating water for temperature control, similar to that described by Butler (10).

Although it has been suggested that each worker prepare his own composition curve, it is believed that direct use of the data recorded here may be made if primary liquids are available which have the same constants as the media employed by the author.

Experimental mixtures which have been prepared to determine the composition curve will, in general, not have indices which conveniently fit into a set having regular intervals of, say, 0.01 or 0.005 (see Table 1). These liquids may be adjusted to a desired index by adding an amount of one constituent determined by a simple calculation as shown in the example below:

Composition of 10 ml. sample of experimental liquid, $n = 1.7134$
$10.0 \times 0.750 = 7.50$ ml. CH_2I_2
$10.0 \times 0.250 = 2.50$ ml. $C_{10}H_7Br$

Composition of liquid, $n = 1.710$ (From curve, Fig. 1)
71.7% CH_2I_2
28.3% $C_{10}H_7Br$

Hence

0.717 V_a = 7.50 ml. CH_2I_2 present in original liquid.

V_a = 10.46 ml. total volume of adjusted liquid.

0.283 V_a = 2.96 ml. $C_{10}H_7Br$ present in adjusted liquid.

Therefore

2.96 − 2.50 = 0.46 ml. of $C_{10}H_7Br$ must be added to the original liquid to bring n to 1.710.

It is assumed in making these calculations that the initial volume of the mixed liquids remains constant and that the solutions are ideal. These assumptions are approximately true if minute drops of liquid are used in determining the indices of initial mixtures and if adjustments are relatively small. The method is superior to adjustment by trial and error.

Purification and Preservation of Methylene Iodide

Methylene iodide is unstable when exposed to light and heat and unless precautions are taken it has a tendency to liberate iodine. The following hypothetical equation may be written to express the decomposition:

$6CH_2I_2$	$\rightarrow$	CH_3I	+	$3CHI_3$	+	I_2	+	C_2H_6
Methylene iodide		Methyl iodide		Iodoform		Iodine		Ethane

Emschwiller (15) has studied the photolysis of methylene iodide and related compounds, but further work is required to demonstrate the true nature of the decomposition with which we are concerned here.

The coloration or opacity which results from the presence of free iodine is undesirable in an immersion liquid. Reinhard Brauns (1), in the original article describing the use of methylene iodide, stated that this substance might be purified by shaking with an aqueous solution of potassium hydroxide. Later authors have mentioned this procedure in connection with the use of methylene iodide as a heavy liquid (G. = 3.3) for mineral separations, but this method of purification has evidently been missed by some who are interested in methylene iodide as an immersion medium.

Schroeder van der Kolk (16) has advised the use of copper to prevent discoloration of methylene iodide and in the writer's opinion this procedure is most satisfactory. However, copper is slow to decolorize methylene iodide; therefore, it is suggested that deeply discolored samples of this substance be shaken with dilute potassium hydroxide solution until the original pale color is restored. The liquid should then be washed with distilled water, dried over anhydrous calcium chloride and filtered. It may then be preserved over clean copper wire or foil which has been previously treated with hydrochloric acid to remove oxidation products

TABLE 1

Index of Refraction, n_D	Vol. % CH_2I_2	Vol. % $C_{10}H_7Br$	Temperature ° C.
1.6587	0.0	100.0	19.7
1.6723	25.0	75.0	20.0
1.6909	50.0	50.0	20.0
1.7134	75.0	25.0	20.0
1.7410	100.0	0.0	19.9

TABLE 2

Index of Refraction, n_D	Vol. % CH_2I_2	Vol. % $C_{10}H_7Br$	Temperature ° C.
1.6606	2.7	97.3	18.3
1.6705	21.3	78.7	18.3
1.6800	36.2	63.8	18.4
1.6893	48.8	51.2	18.5
1.7001	60.3	39.7	18.3
1.7102	70.7	29.3	18.5
1.7202	80.6	19.4	18.4
1.7302	90.0	10.0	18.2
1.7402	99.1	0.9	18.3

TABLE 3

1 Calculated Index of Refraction (Equation 3)	2 Observed Index of Refraction (See Table 2)	3 Index of Refraction (Corrected to 20° C.)	4 Difference (Column 1 and 3)
1.6599	1.6606	1.6598	.0001
1.6700	1.6705	1.6696	.0004
1.6800	1.6800	1.6791	.0009
1.6896	1.6893	1.6884	.0012
1.6995	1.7001	1.6991	.0004
1.7092	1.7102	1.7092	.0000
1.7192	1.7202	1.7191	.0001
1.7294	1.7302	1.7290	.0004
1.7399	1.7402	1.7390	.0009

or tarnish. If the copper is renewed occasionally, the discoloration of the methylene iodide will be avoided.

The use of tin and mercury advocated by some is not recommended.

J. W. Retgers (17) has shown that stannic iodide is soluble in methylene iodide and qualitative tests by the writer have shown the presence of mercury in a filtered sample of methylene iodide which previously had stood over this metal.

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References

1. Brauns, R., Ueber die Verwendbarkeit des Methylenjodids bei petrographischen und optischen Untersuchungen: *Neues Jahrb. Mineral.* (II), 72–78 **(1886).**
2. Schroeder van der Kolk, J. L. C., *Kurze Anleitung zur mikroskopischen Krystallbestimmung*, 12–13, Wiesbaden **(1898).**
3. Wright, F. E., *The Methods of Petrographic-Microscopic Research*, Carnegie Inst. Pub. **158,** 98 (1911).
4. Larsen, E. S., and Berman, H., The Microscopic Determination of the Nonopaque Minerals, 2nd ed.: *U. S. Geol. Surv., Bull.* **848,** 12 (1934).
5. Anderson, B. W., and Payne, C. J., Liquids of high refractive index: *Nature,* London, **133,** 66–67 (1934).
6. Zirkel, F., *Lehrbuch der Petrographie*, 2nd ed., I, 40 **(1893).**
17. West, C. D., Immersion liquids of high refractive index: *Am. Mineral.*, **21,** 245–249 (1936).
8. Brunn, B., and Barth, T. F. W., Stability on storage of the high index liquids of C. D. West: *Am. Mineral.*, **32,** 92 (1947).
9. Mayrhofer, A., Über Immersionsflüssigkeiten zur Bestimmung des Brechungsvermögens fester Körper nach dem Einbettungsverfahren: *Mikrochemie*, **9,** 52–71 (1931).
10. Butler, R. D., Immersion liquids of intermediate refraction (1.450—1.630): *Am. Mineral.*, **18,** 390 (1933).
11. Buerger, M. J., The optical properties of ideal solution immersion liquids; *Am. Mineral.*, **18,** 325–334 (1933).
12. Kaiser, E. P., and Parrish, W., Preparation of immersion liquids: *Ind. Eng. Chem., anal. ed.*, **11,** 560–562 (1939).
13. Rogers, A. F., and Kerr, P. F., *Optical Mineralogy*, 2nd ed., McGraw-Hill Book Co., Inc., New York **(1942).**
14. Mayrhofer, A., and Wratschko, F., Bemerkungen zur Berechnung des Brechungsvermögens von gemischten Immersionsflüssigkeiten: *Pharmazeutische Presse, Wissenschaftliches-praktisches Heft*, 33–35 **(1931).**
15. Emschwiller, G., L'action chimique de la lumière sur les dérivés diiodés des carbures d'hydrogene; diiodoéthanes, diiodométhane: *Compt. rend.*, **199,** 854–856 (1934).
16. Schroeder van der Kolk, J. L. C., *Tabellen zur microskopischen Bestimmung der Mineralien*, 13, Wiesbaden **(1900).**
17. Retgers, J. W., Ueber das Krystallsystem des Zinnjodids: *Zeit. Kryst.*, **22,** 271 (1894).