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THE OPTICAL PROPERTIES OF IDEAL SOLUTION IMMERSION LIQUIDS

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ABSTRACT

Immersion technique requires a series of liquid standards of continuously variable optical properties. These are provided by mixing end members of different index. One particular case of miscible liquid pairs, known as ideal solutions, provides simple relations between composition and optical properties. In an ideal solution system, index is a linear function of composition, and it is shown, from this and other considerations, that it follows that the temperature coefficient and dispersion are linear in composition and also in index. This enables the index of the entire system of liquid solutions at all wavelengths to be given on a single straight line chart.

INTRODUCTION

Emmons has proposed sets of liquids[1,2,3] which are suited to the requirements of the variation methods, in which absolutely reproduceable optical properties are necessary. So long as this constancy is attainable and the liquids are reasonably convenient to use, and so long as liquids are available so that their variation ranges overlap somewhat, the optical properties of individual liquids and their mutual relationships are immaterial. When the liquid standards are to be used for ordinary immersion technique, however, there are other considerations worth taking into account in designing a set of liquids. For ordinary technique, a set of liquids ought to have the following property which, incidentally, would add convenience to the liquids to be used in the double variation technique if optical constancy could be simultaneously secured:

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[1] R. C. Emmons, The double dispersion method of mineral determination (preliminary paper): *Am. Mineral.*, **13,** 1928, pp. 504–515.

[2] R. C. Emmons, The double variation method of refractive index determination (second paper): *Am. Mineral.*, **14,** 1929, pp. 414–426.

[3] R. C. Emmons, A set of thirty immersion media: *Am. Mineral.*, **14,** 1929, pp. 482–483.

The primary desideratum is that adjacent liquids should have nearly, if not quite, identical optical properties other than index. For example, in some of the older sets of immersion liquids made up of various oils, cinnamon oil gave trouble because of its enormous dispersion. The colored fringes formed in white light by oblique illumination tests always gave erroneous impressions, in comparison with adjacent liquids, as to the difference between liquid and crystal indices. In other words, with this kind of a series of immersion liquids, the nearness to a match in indices cannot be reliably inferred from the oblique illumination test. The most desirable situation would be to have a series of liquids of different refractions but equal dispersions and temperature coefficients. Unfortunately, however, substances with low indices as a rule have relatively low dispersions while substances with high indices have high dispersions. To a less marked extent the same relationship holds with regard to temperature coefficients as well. An ideal immersion series is therefore not attainable. It is not difficult, however, to make a series of liquids of different refractions, having dispersions and temperature coefficients continuously variable with refractive index. This allows comparable oblique illumination tests with liquids of not too widely separated index, a feature not only of convenience to the veteran crystallographer, but also of the greatest importance to the beginning student, who has plenty to occupy his attention without having to keep in mind the details of a discontinuous dispersion series. This requirement calls for a series of liquids, in its simplest form, made by mixing two miscible end members of as widely different index as feasible. In the following section, the relationship between properties in such a series will be given.

THE OPTICAL PROPERTIES OF IDEAL SOLUTIONS

Ideal Solutions

In a system of liquid solutions derived by dissolving two mutually miscible end members in one another, the physical properties of intermediate mixtures are necessarily continuous functions of composition. The form of the function may vary from case to case. One very simple, particular kind of solution system may, however, be distinguished; this is to be designated an *ideal solution* system. An ideal solution system is one in which the form of the above function is linear. In other words, in a series of individual ideal solutions made from two end members, the properties of intermediate members are straight line functions of composition. The physical significance of this is that in an ideal solution, the molecules of each of the constituents function as if they were independent, and properties are additive. Fundamentally, a molecule, placed in a series of environments, will behave as if it were independent of its environment if these are chemically and physically similar, and give rise to the same "background" interaction with the molecule in question. Hence mixtures of chemically very similar liquids give rise to ideal solutions.

REFRACTIVE INDEX

The refractive indices of possible intermediate members of an ideal liquid-liquid solution system are indicated graphically in Fig. 1. The two end members A, and B, have indices n_A and n_B respectively. The index n_x of any mixture of A and B depends on the relative proportions by volume, V_A and V_B, of A and B present in the total volume V. From the similar triangles, the precise relation can be seen to be:

$$\frac{n_x - n_A}{n_B - n_A} = \frac{V_B}{V_B + V_A} = \frac{V_B}{V} \tag{1}$$

or

$$n_x = n_A + \frac{V_B}{V_B + V_A}(n_B - n_A). \tag{2}$$

Given, then, two end members of indices n_A and n_B, and a bottle holding V cc. of liquid, it is possible to calculate the volume of A and the volume of B to add to it to fill it with a liquid of index n_x. The volume is usually set at about 16 cc. by the standard double stoppered bottles (which have an average volume of 20 cc. but vary between 18–25 cc.). In the original standardization procedure, the volumes V_A and V_B are conveniently run directly into the bottle from a couple of sensitive burets. The bottle is then stoppered with the first stopper, shaken thoroughly, and the index of the liquid checked exactly on a refractometer.

Due to the impossibility of reading a buret closer than a drop, sufficient precision can be had by graphical calculation. This is conveniently accomplished by drawing Fig. 1 to a large scale on graph paper so that the base line is equal to 16 cc. The volumes of A and B to be added for any liquid X are then given directly.

If the end members are miscible but do not form ideal solutions, the properties of intermediate members lie on a curve such as the dotted line in Fig. 1. If a graph is available beforehand, intermediate members may be made up rapidly.

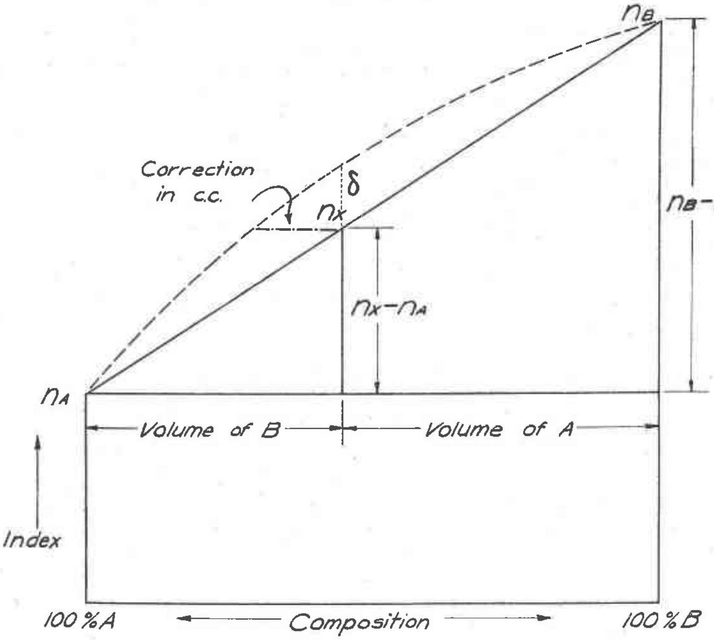

FIG. 1

TEMPERATURE COEFFICIENT

In Fig. 1, the index line n_A n_x n_B applies, of course, to indices taken at any wavelength or at any temperature, because, for ideal solutions, all properties are straight line functions of composition without restriction. It follows that the vertical *difference* between the straight line representing indices, say, at 20°C., and the straight line representing indices at 21°C., will be a third straight line which might be labelled $n_{20} - n_{21}$. That is to say, the temperature coefficient of refractive index, dn/dT, is a linear function of composition. Since composition and index are linear with respect to one another, and composition and temperature coefficient are linear with respect to one another, it follows that index and temperature coefficient are also linearly related. In other words, the temperature coefficient of refractive index of an ideal solution system is a straight line function of index.

Composition can be measured by either weight or volume methods. The first is accurate but inconvenient, and the second is convenient but limited by the accuracy of the buret. In practical cases, a total volume of 16 cc. is dealt with, and a buret can be run and read to about 0.1 cc. This gives an accuracy of the order of 1%. Index, however, can be rapidly and certainly read to about 0.0001. For an index range of the order of $1.5000-1.4000=.1000$, an accuracy of the order of 0.1% can be attained. Therefore, in the making and standardization of index liquids, it is desirable to make rough approximations to correct value by volume and final checks by means of refractive index directly. It is for this reason that attention is given above to the interchangeability of composition and index as a coordinate with which to compare temperature coefficient (and dispersion, see below).

DISPERSION

Similarly, for any constant temperature, a straight line would represent the index as a function of composition at some wavelength λ_1, while another straight line would represent it at another wavelength λ_2. The difference between these two indices is a third straight line relating $n_{\lambda 1}-n_{\lambda 2}$ to composition. In other words, the dispersion $\Delta n/\Delta\lambda$ is a linear function of composition, and following the reasoning in the last section, it is also a straight line function of index. This, of course, applies not only to the arbitrary dispersion n_F-n_C, but to any other dispersion whatever. It will be convenient to use the dispersion n_x-n_D in certain practical cases to be discussed.

The dispersion of a substance can be derived from any one of several formulas which give refractive index as a function of wavelength. For the present purpose, the empirical Hartmann formula, which represents indices well, will be employed. This is:

$$n = n_0 + \frac{c}{(\lambda_0 - \lambda)^k} \qquad (3)$$

where n is the index desired for wavelength λ, and where n_0 is the index at some arbitrary standard wavelength λ_0; k is a constant which is practically invariable from substance to substance. For glass, it is usually taken as 1.2. Certainly it can be taken as identical for two liquids which form near-ideal solutions. It is this circumstance which brings about a very great convenience in the use of an ideal solution system for immersion media.

Relation (3) may be expressed:

$$n - n_0 = \frac{c}{(\lambda_0 - \lambda)^k} \tag{4}$$

or more simply:

$$-\Delta n_A = \frac{c}{(\Delta\lambda)^k} \tag{5}$$

where Δn_A is the change in refractive index of a liquid, A, as measured from some standard index, corresponding with the change in wavelength, $\Delta\lambda$, from some standard wavelength. This is illustrated in Fig. 2. A similar relation holds for any second liquid, B, of the same ideal solution system for the same change in wavelength, $\Delta\lambda$:

$$-\Delta n_B = \frac{c'}{(\Delta\lambda)^k} \cdot \tag{6}$$

Dividing (6) by (5) gives:

$$\frac{\Delta n_B}{\Delta n_A} = \frac{c'}{c} \cdot \tag{7}$$

That is to say, at any wavelength whatever, the ordinate of the dispersion curve of a liquid, B, is a magnified version of the ordinate of the dispersion curve of another liquid, A, the magnification ratio being c'/c. Consequently, all dispersion curves are identical with one another except for the scale of the ordinates. This, of course, is not generally true for any two substances whatever, but it is true so long as the constant k in the Hartmann dispersion formula is really a constant. This is the case with pair of liquids capable of forming ideal solutions, as will be demonstrated with an actual example in a following paper.[4]

The foregoing relationships may now be combined into a single diagram from which the dispersion of any solution of an ideal solution system may be read, having given the index of the solution in question for any wavelength. Since the effective wavelength of the

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[4] R. D. Butler, Immersion liquids of intermediate refraction, to follow.

light from a sodium flame has come to be the standard for which refractive indices are usually given, both in the literature and on certain calibrated refractometers (say, the Abbe refractometers, which are so popular), n_D, will be chosen as the standard n_0 of equation (3), which thus makes $\lambda_0 = \lambda_D$. The upper left drawing of Fig. 2 shows the dispersion curves of two end member liquids, A and B. According to the preceding discussion, the height of the ordinate at any wavelength referred to the height of the ordinate at the standard wavelength, λ_D, as zero, is the same in each liquid except for the scale of the ordinate system. Hence all rays drawn through the ordinates of corresponding points on the curves of liquids A and B will meet in a point which may be termed the *projection* point. According to the discussion the dispersion of any intermediate member made by mixing the two end members, A and B, is also a linear function of the index of the mixture. If the scale of the distance between the planes of the dispersion curves of A and B (Fig. 2) is given the dimension of index, then the ray system through the ordinates of the dispersion curves for liquids A and B will intersect the plane of the dispersion curve of the mixture and determine a dispersion curve whose ordinate scale is proportional to the distance of the new plane from the point of projection. Thus the end members and all possible intermediate members of an ideal solution system have dispersion curves whose corresponding ordinates are proportional to a constant plus n_D, the constant being the distance of the point of projection (in terms of refractive index) to the index of the lower index end member.

For practical use, this space diagram must be drawn in two dimensions. The construction is indicated in the lower half of Fig. 2. The wavelength scale is obtained from a carefully explored dispersion curve near the high index end of the system. A second partially explored curve locates a few points which determine the projection point. The wavelength scale is most accurately constructed by plotting the indices of points of the well explored curve, not on ordinary graph paper, but on special Hartmann dispersion formula graph paper,[5] on which dispersion curves come out as striaght lines (see Fig. 6 of reference 4). This allows very accurate interpolation and especially extrapolation for the construction of scales. Actually there is a slight curve in the dispersion lines even on this paper,

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[5] Apparently unknown in America, but obtainable from Germany through E. Leitz, Inc., 60 East 10th St., New York.

due probably to the fact that the constant k is not quite correct for liquids. This error, however, can be eliminated by smoothing in a curve which is very near to the straight line but which fits the experimental points a little better.

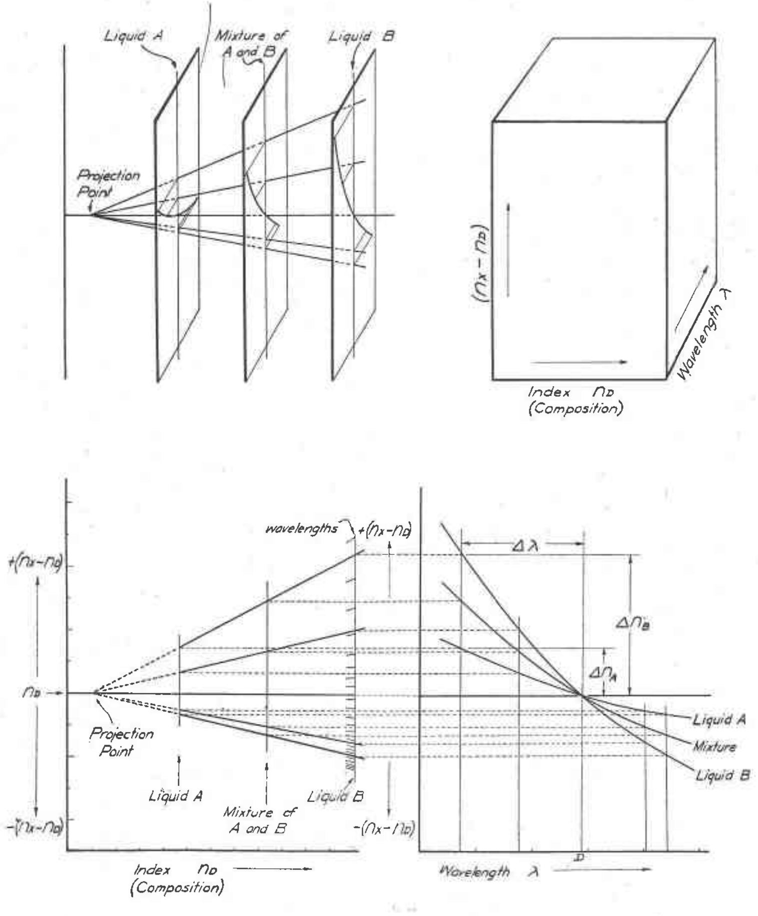

FIG. 2

To use the diagram, proceed as follows: Given a liquid in the system, whose index has been determined for sodium light at some standard temperature, to find its index at any other wavelength: On the lower left diagram (which is the only useful part of the diagram, after it has been constructed), draw a vertical line corresponding with the index n_D. Lay a straight edge from the projection point to the point on the wavelength scale on the right hand side

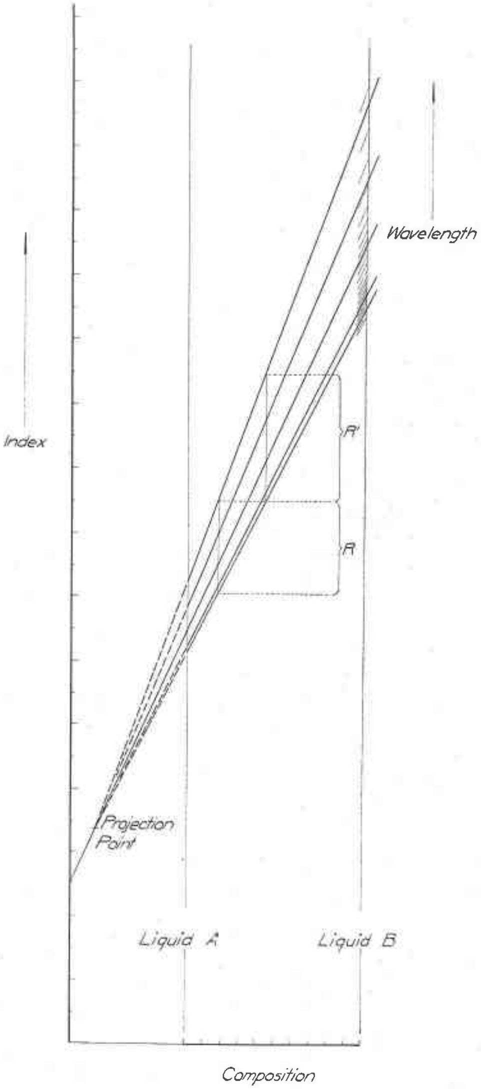

FIG. 3

of the diagram, corresponding to the wavelength for which the index is required. The ordinate of the point of intersection of the line and the straight edge, as read on the left border, gives the corection to be algebraically added to n_D to give the required index.

The above described chart is essentially one giving *corrections* to be applied to the sodium index of any liquid in order to get its index at any other wavelength. Being a correction chart it is very economical of space. If desired, however, the corrections may be made to apply themselves automatically by extending the chart and modifying it as shown in Fig. 3. Here, the baseline is not zero, but the actual index of the liquid, which is, of course, variable with composition. It corresponds with the previous Fig. 2, then, except that the sodium index line which is there horizontal, is arranged to follow the actual index of the liquid system as given in Fig. 1. In other words, Fig. 2 has been sheared counterclockwise until the n_D line acquires its actual slant.

The following point should be observed: The abscissae of Fig. 3 are correctly assigned the dimensions of composition. As explained previously, however, the actual composition of the liquid is only dealt with approximately during the preliminary stages of mixing the liquids. From this stage forward, composition is of no interest whatever, for optical properties alone are of use and measureable. Therefore, the units of composition may be omitted from the chart, and the n_D line given whatever slant is necessary for the accuracy of index desired. If the scale of indices is to be made accurate, this chart takes up a great deal of space.

From this chart, the index range covered by a given liquid with wavelength variation is given by the length of a vertical line at the composition abscissa corresponding with that liquid, which is intercepted by the wavelength range to be used. In Fig. 3, R is the index range of the liquid whose composition corresponds with the left hand short vertical line. If a set of liquids is to be designed so that each liquid begins its range where its neighbor leaves off, this can be conveniently done by the aid of the chart, as indicated by the non-overlapping ranges R and R'. Any desired overlap can be easily arranged for in similar fashion.

The writer is indebted to Mr. R. D. Butler for drawing the illustrations to his specification. In a following paper, by R. D. Butler, the optical properties of an actual ideal solution series will be described.