

SOME PROPERTIES OF α -MONOCHLORONAPHTHALENE-DIIODOMETHANE IMMERSION MEDIATAKASHI FUJII AND F. DONALD BLOSS, *Department of Geology, Southern Illinois University.*

ABSTRACT

The density and refractive index for various blends of diiodomethane (methylene iodide) and α -monochloronaphthalene were measured at 15.0, 20.0, 22.0, 25.0, and 30.0° C. Little deviation from ideality was detectable for the series if density was plotted against volume fraction or if specific volume was plotted against weight fraction. However, a plot of the thermal expansion coefficients versus volume fraction showed significant deviation from linearity and therefore demonstrated the solutions to be non-ideal. Plots of refractive index against composition, regardless of the compositional units used, resulted in non-linear curves. The relation between refractive index, density, and composition in weight fractions for the series most closely conforms to the Lorentz-Lorenz equation, almost as well to the Lichteneker equation, but increasingly less satisfactorily to the Gladstone-Dale, Newton-Drude, and Allen equations. The relation between refractive index and density for this series is non-linear in contrast to what is commonly thought.

For solutional series in general, refractive index and density are linearly related only if

$$\left(\frac{\partial \rho}{\partial n}\right)_c = \left(\frac{\partial \rho}{\partial n}\right)_t$$

(refractive index being here considered as just a function of composition and temperature). In the event of such linearity, this line will be independent of temperature. Only those thermodynamically ideal solutions for which this is true will correspond to the "optically ideal" solutions of earlier workers. "Optical ideality" and a linear relation between refractive index and density should thus be infrequently encountered.

The dispersion, $n_F - n_C$, for blends of diiodomethane and α -monochloronaphthalene is not linearly related to composition (regardless of the compositional units chosen). When $n_F - n_C$ is plotted against n_D , a non-linear relation is also demonstrated for this series. However, if specific dispersion, $(n_F - n_C)/\rho$, is plotted against volume fraction, the result is almost linear as would be expected from the Gladstone-Dale equation.

INTRODUCTION

Refractive index liquids, as long recognized, may also be used in specific gravity determinations. Foster (1947) points out that a blended series of such media serves as "a ready-made series of specific gravity standards" and moreover, if properly selected, will permit "close calibration of specific gravity through measurement of the refractive index. . . ." The blended series between α -monochloronaphthalene and diiodomethane (although admittedly less accurate for measuring density than the solutions of Clerici, Klein, Thoulet or Rohrbach) has the double advantage of being relatively innocuous and also readily available in most petrographic laboratories. However, to the writers' knowledge, no recent data which relate density and refractive index for blends of this series are readily available to petrographers and mineralogists. Foster's curve

(1947, Fig. 2), in the absence of experimental data, assumed the relation to be linear for this series. Theoretical considerations, however, led the writers to suspect non-linearity and the following study was undertaken.

Blends of recently purchased stocks of α -monochloronaphthalene and diiodomethane were made to the volumetric specifications of Kaiser and Parrish (1939) in order to determine, as an incidental to this study, how closely these blends might conform in refractive index to those of twenty years ago. Density measurements on these blends indicated a closely linear relation between volume fraction and density, but, as in previous studies (N. W. Buerger, 1933; Kaiser and Parrish, 1939), a non-linear relation between refractive index and volume fraction. Thus the relation between refractive index and density for this series was expectably non-linear.

EXPERIMENTAL PROCEDURES

Density measurement Densities of α -monochloronaphthalene and diiodomethane were measured with a 10 cc. pycnometer whose volume had been calibrated at 15.0°, 20.0°, 22.0°, 25.0° and 30.0° C., from the known density of distilled water at these temperatures (Daniels *et al.*, 1956, p. 474). A thermometer built in the ground glass stopper of the pycnometer (and projecting deep within the pycnometer's contents when the stopper was inserted) permitted temperature measurement to $\pm 0.1^\circ$ C. The pycnometer and its contents were brought to the desired temperature by their insertion into a beaker which itself had been immersed (almost up to its lip) in a regulated constant temperature bath. Due caution was maintained to keep the outside of the pycnometer clean and dry during this operation. Anomalous density measurements were obtained for diiodomethane, if during cooling, its temperature dropped below 10° C. In such an event, the solution was observed to become turbid, perhaps because of the formation of one of the three unstable forms of diiodomethane observed by Deffet (see Timmerman, 1950).

Using the densities measured at 22° C. for pure α -monochloronaphthalene and diiodomethane (purchased in October 1959 from Distillation Products Industries), the volume percentages in Table 1, which are those cited for several of the blends studied by Kaiser and Parrish (1939, p. 561, Table III), were converted to weight per cents. Samples 2 to 7 (Table 1) were then prepared gravimetrically to reproduce, as closely as possible, the compositions studied by Kaiser and Parrish. The densities of these blends were then measured at 15.0°, 20.0°, 22.0°, 25.0°, and 30.° C using the precautions discussed in the preceding paragraph. Results are summarized in Table 1.

Refractive index measurement Refractive indices of the pure end mem-

TABLE 1. REFRACTIVE INDEX AND DENSITY MEASUREMENTS FOR DIODOMETHANE- α -MONOCHLORONAPHTHALENE MIXTURES

Sample Number	Concentration of Diiodomethane			Kaiser and Parrish n_D (22° C.) ¹	Measured Densities and Refractive Indices														
	Mol %	Wt. %	Vol. %		22° C.			15° C.			20° C.			25° C.			30° C.		
					n_D	ρ	n_D	ρ	n_D	ρ	n_D	ρ	n_D	ρ	n_D	ρ			
1	0.0	0.0	0.0	1.633	1.6320 ±0.0006	1.1926 ±0.0002	1.6350 ±0.0004	1.1978 ±0.0002	1.6328 ±0.0005	1.1941 ±0.0001	1.6307 ±0.0007	1.1903 ±0.0003	1.6287 ±0.0004	1.1860 ±0.0001					
2	26.8	37.6	17.8	1.645	1.6432 ±0.0002	1.5593 ±0.0003	1.6467 ±0.0002	1.5668 ±0.0004	1.6444 ±0.0005	1.5614 ±0.0004	1.6418 ±0.0002	1.5560 ±0.0004	1.6392 ±0.0008	1.5502 ±0.0004					
3	48.2	60.4	35.3	1.660	1.6572 ±0.0002	1.9277 ±0.0003	1.6617 ±0.0004	1.9377 ±0.0003	1.6589 ±0.0003	1.9304 ±0.0003	1.6558 ±0.0002	1.9234 ±0.0002	1.6529 ±0.0009	1.9162 ±0.0004					
4	63.1	73.7	50.2	1.675 ²	1.6728 ±0.0008	2.2408 ±0.0001	1.6776 ±0.0006	2.2522 ±0.0003	1.6744 ±0.0008	2.2440 ±0.0003	1.6705 ±0.0002	2.2358 ±0.0001	1.6669 ±0.0007	2.2261 ±0.0002					
5	74.1	82.5	62.9	1.690	1.6864 ±0.0003	2.5097 ±0.0005	1.6912 ±0.0005	2.5235 ±0.0002	1.6874 ±0.0004	2.5136 ±0.0004	1.6839 ±0.0002	2.5044 ±0.0006	1.6806 ±0.0007	2.4939 ±0.0006					
6	83.8	89.4	75.2	1.705	1.7018 ±0.0002	2.7733 ±0.0006	1.7074 ±0.0004	2.7877 ±0.0002	1.7034 ±0.0003	2.7773 ±0.0006	1.6998 ±0.0008	2.7666 ±0.0006	1.6962 ±0.0007	2.7549 ±0.0006					
7	91.5	94.8	86.7	1.720	1.7166 ±0.0002	3.0240 ±0.0006	1.7232 ±0.0003	3.0401 ±0.0002	1.7188 ±0.0002	3.0287 ±0.0006	1.7140 ±0.0006	3.0172 ±0.0005	1.7098 ±0.0009	3.0048 ±0.0005					
8	100.0	100.0	100.0	1.739	1.7364 ±0.0006	3.3176 ±0.0005	1.7420 ±0.0003	3.3344 ±0.0002	1.7383 ±0.0003	3.3225 ±0.0005	1.7340 ±0.0002	3.3100 ±0.0004	1.7298 ±0.0006	3.2962 ±0.0004					

¹ On basis of Kaiser and Parrish (1939) data.² For 50.1% (vol.).

bers and of the six blends were measured at 15.0°, 20.0°, 22.0°, 25.0°, and 30.0° C. by Fujii using the same Abbe prism refractometer (1.45–1.84) that had previously been calibrated by Fisher (1958). The wavelengths used for the measurements were Hg 4358 Å, Hg 5461 Å, Hg 5780 ± 10 Å and Na_D 5893 Å, respectively. During the measurements, temperature was controlled to within ±0.1° C. The precautions suggested by Fisher were observed in detail. Indices measured with sodium light (n_D) are summarized in Table 1. It will be seen that the indices measured at 22.0° C. are lower than those of Kaiser and Parrish.

RELATION BETWEEN DENSITY AND COMPOSITION

For an ideal solution series the relation between density and composition depends on the choice of compositional units, formulas for the interconversion of these latter being summarized in Table 2. If composition is expressed in mole fractions, the relation is non-linear except for the special case wherein the molar volumes of the components happen to be equal or nearly equal (Bloss, 1952). If composition is expressed in volume fractions, the relation is linear (Fujii, 1960); however, the use of volume fractions is neither conventional nor practical, particularly for liquid solutions in which volume fraction may change significantly with temperature. The relation between the reciprocal of the density—that is, the specific volume—and composition in weight fractions is also linear. Thus

$$\frac{1}{\rho} = \frac{1}{\rho_A} w_A + \frac{1}{\rho_B} w_B + \frac{1}{\rho_C} w_C + \dots \quad (1)$$

where ρ is the density of the solution; $\rho_A, \rho_B, \rho_C \dots$ are the densities of

TABLE 2. EQUATIONS FOR INTERCONVERSION OF CONCENTRATIONAL EXPRESSIONS IN IDEAL SYSTEMS¹

Conversion to:		
Mole Fraction (N_i)	Weight Fraction (w_i)	Volume Fraction (v_i)
$N_i = \frac{M}{M_i} w_i$ (a)	$w_i = \frac{M_i}{M} N_i$ (c)	$v_i = \frac{V_i}{V} N_i$ (e)
$N_i = \frac{V}{V_i} v_i$ (b)	$w_i = \frac{\rho_i}{\rho} v_i$ (d)	$v_i = \frac{\rho}{\rho_i} w_i$ (f)

¹ Equations (a) and (c) can also be used for non-ideal systems. $M, V,$ and ρ represent the molecular weight, molar volume, and density of a solution between two or more end members and $M_i, V_i,$ and ρ_i represent the molecular weight, molar volume, and density of an end member of this solution series.

TABLE 3. PERCENTAGE VOLUME INCREASE PRODUCED BY MIXING OF α -MONOCHLORONAPHTHALENE AND DIODOMETHANE

Sample	Mixing Temperature				
	15°	20°	22°	25°	30°
2	0.71	0.73	0.74	0.75	0.75
3	0.72	0.77	0.78	0.80	0.79
4	0.82	0.85	0.86	0.87	0.79
5	0.71	0.76	0.78	0.77	0.80
6	0.60	0.63	0.63	0.65	0.67
7	0.33	0.35	0.36	0.36	0.37

its components; and w_A , w_B , w_C , are the weight fractions of these components in the solution.

Solutions of diiodomethane in α -monochloronaphthalene appeared to be ideal at first glance since, for this series, an almost linear relation existed between density and composition in volume fractions (or between specific volume and composition in weight fractions). However, the volume of each blend, as calculated from its weight and density, consistently exceeded the sum of the volumes of its two components (Table 3). These slight deviations from additivity of volume thus indicated the system α -monochloronaphthalene–diiodomethane to deviate somewhat from ideality.

EFFECT OF TEMPERATURE ON DENSITY

A definite relationship exists between the rate of change of density with temperature (*i.e.*, $d\rho/dt$) for a substance and its coefficient of thermal expansion (α). This relation can be derived from the definition of α ,

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial t} \right)_p, \quad (2)$$

by substitution of M/ρ for the volume term V (t , p , and M represent temperature, pressure, and mass). Since mass is constant with temperature, eq. (2) becomes

$$\alpha = - \left(\frac{\partial \ln \rho}{\partial t} \right)_p. \quad (3)$$

Eq. (3) indicates that if $\ln \rho$ is plotted against temperature for a given substance, the slope of the curve at any selected temperature point equals $-\alpha$ in value for that temperature. If this is done for solutions 1, 4, and 8 of Table 1, curves 1, 4, and 8 in Fig. 1 result. (Similar graphs

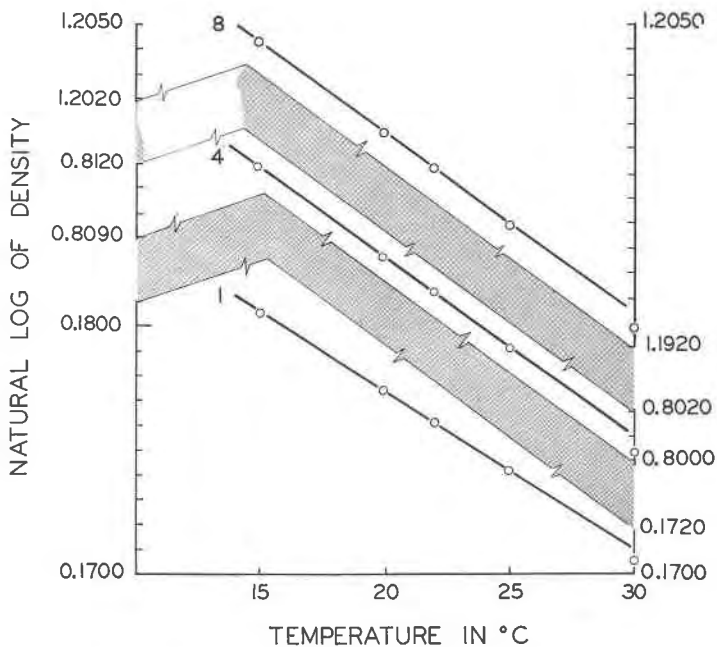


FIG. 1. Variation of $\ln \rho$ with temperature for pure α -monochloronaphthalene (sample 1), for pure diiodomethane (sample 8), and for a solution between them (sample 4).

were made for solutions 2, 3, 5, 6, and 7.) In all such graphs, linearity existed between 15 and 25° C. whereas between 25° and 30° C. the slope changed. From the slope between 15 and 25° C., α_D and α_α , the coefficients of thermal expansion for pure diiodomethane and α -monochloronaphthalene in this temperature range, were determined as 7.3×10^{-4} and 6.3×10^{-4} , respectively. Results for all the liquids studied are summarized in Table 4. Beyond the 15–25° C. range the coefficients of thermal expansion may not be, relatively speaking, so independent of temperature.

For a series of ideal solutions, the coefficients of thermal expansion are linearly related to composition in volume fractions (Fujii, 1960, p. 380). For the system α -monochloronaphthalene–diiodomethane this is obviously untrue (Fig. 2). In contrast with plots of density against weight fraction, it appears that non-ideality can be detected with considerable sensitivity by plotting the coefficients of thermal expansion against volume fractions for a series of solutions.

In an ideal system, the value of $d\rho/dt$ is linearly related to composition in volume fractions only if α has the same value for all solutions of the

TABLE 4. COEFFICIENTS OF THERMAL EXPANSION AND OF $d\rho/dt$ FOR α -MONOCHLORONAPHTHALENE-DIIODOMETHANE SOLUTIONS WITHIN THE RANGE 15–25° C.

Sample	α	$-d\rho/dt$
1	$6.3 \times 10^{-4} \pm 0.00003$	7.5×10^{-4}
2	$6.9 \times 10^{-4} \pm 0.00004$	10.8×10^{-4}
3	$7.4 \times 10^{-4} \pm 0.00004$	14.2×10^{-4}
4	$7.3 \times 10^{-4} \pm 0.00003$	16.4×10^{-4}
5	$7.7 \times 10^{-4} \pm 0.00006$	19.3×10^{-4}
6	$7.6 \times 10^{-4} \pm 0.00006$	21.2×10^{-4}
7	$7.6 \times 10^{-4} \pm 0.00006$	22.9×10^{-4}
8	$7.3 \times 10^{-4} \pm 0.00005$	24.4×10^{-4}

series. To derive this relationship, differentiate Fujii's equation (1960, p. 380)

$$\rho = \sum \rho_i v_i \quad (4)$$

with respect to temperature (pressure remaining constant) to obtain

$$\left(\frac{\partial \rho}{\partial t}\right)_p = \sum v_i \left(\frac{\partial \rho_i}{\partial t}\right) + \sum \rho_i \left(\frac{\partial v_i}{\partial t}\right)_p. \quad (5)$$

As eq. (5) indicates, a linear relationship between $(\partial \rho / \partial t)_p$ and volume fraction v_i is possible for a solution series only if $(\partial v_i / \partial t)_p$ equals zero. This occurs only for the very specialized case wherein α , the thermal coefficient of the solution, is equal to α_i , that of its i th component. To prove this, let v_i and V_i respectively represent the volume fraction and total volume of the i th component in a solution whose volume is V . By definition of volume fraction

$$v_i = \frac{V_i}{V}. \quad (6a)$$

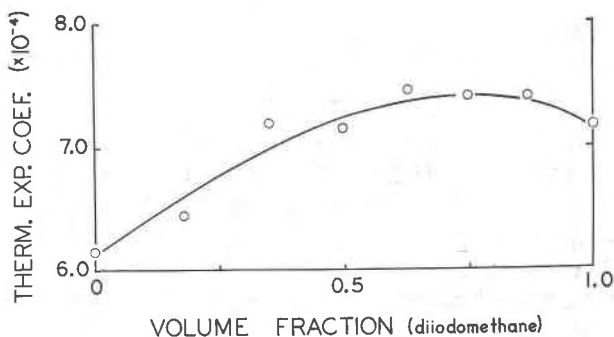


FIG. 2. Variation of the coefficient of thermal expansion (α) with respect to volume fractions of diiodomethane for solutions of the α -monochloronaphthalene-diiodomethane series within the 15–25° C. temperature range.

Differentiating eq. (6a) with respect to temperature we obtain

$$\left(\frac{\partial v_i}{\partial t}\right)_p = \frac{V \left(\frac{\partial V_i}{\partial t}\right) - V_i \left(\frac{\partial V}{\partial t}\right)_p}{V^2} \quad (6b)$$

From eq. (2) it is apparent that

$$\left(\frac{\partial V_i}{\partial t}\right) = V_i \alpha_i \quad \text{and} \quad \left(\frac{\partial V}{\partial t}\right)_p = V \alpha.$$

Substituting these into eq. (6b) there results

$$\left(\frac{\partial v_i}{\partial t}\right)_p = \frac{V_i}{V} (\alpha_i - \alpha). \quad (7)$$

It is now obvious that $(\partial v_i / \partial t)_p$ can equal zero only when α_i equals α . For the system studied α_D and α_α differ significantly in value and, as observed, $d\rho/dt$ is thus not linearly related to volume fractions of diiodomethane (Table 4).

REFRACTIVE INDEX AND COMPOSITION

Non-linearity of the refractive indices with volume per cent composition in the α -monochloronaphthalene-diiodomethane system was reported by N. W. Buerger (1935) and later corroborated by Kaiser and Parrish (1939). The present results indicate the refractive index to be non-linear with composition represented by volume fraction, mole fraction, or weight fraction.

The nature of the variation of refractive index with composition in solutions, glasses, and solid solutions has been studied extensively (Tilley, 1922; Porter, 1925; Barth, 1930; Sun *et al.*, 1940). According to Barth (1930), Mallard in 1885 developed the following equations

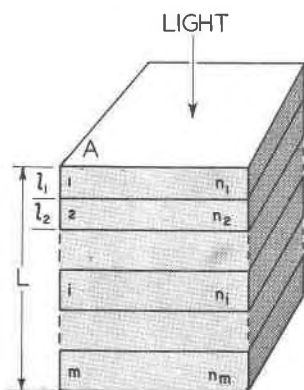
$$n = n_1 N_1 + n_2 N_2 \quad (8)$$

and

$$\frac{1}{n^2} = \frac{N_1}{n_1^2} + \frac{N_2}{n_2^2} \quad (9)$$

where n_1 and n_2 represent the refractive indices of two transparent, miscible materials, n the index of their mutual solution, and N_1 and N_2 the mole fractions of each in this solution. Eq. 8, which is frequently used by mineralogists and petrographers, was developed by analogy to the superposition of two isotropic plates of differing indices.

This same approach may be used to develop an equation of which eq. (8) is a special case. If, for example, the m components of a solution were to become stratified (Fig. 3) then d , the optical path for normally incident light passing through this solution, would be the sum of the optical paths for the individual strata, *i.e.*



A: area of plate

FIG. 3. Hypothetical stratification of a solution into pure layers of its components. For these individual layers, l and n represent thickness and refractive index, respectively.

$$d = \sum_i^n n_i l_i$$

where n_i and l_i represent refractive index and thickness of each individual layer. If z represents the time necessary to pass through the strata, then the velocity of the light in a vacuum is $\sum n_i l_i / z$ whereas its average velocity through the plates is $\sum l_i / z$. Thus, the index of refraction of the superposed strata is

$$n = \frac{\sum n_i l_i}{\sum l_i}$$

As Fig. 3 indicates, however, since the interfaces between the strata are of equal area (A), the ratio of the thickness of an individual plate to the sum of all thicknesses equals v_i , its volume fraction in the solution *i.e.*,

$$\frac{l_i}{\sum l_i} = v_i$$

and, consequently,

$$n = \sum n_i v_i \quad (10)$$

Eq. (10), previously derived by Tillotson (1918), has been used by several workers (M. J. Buerger, 1933; Gibb, 1942; Kerr, 1960). Binary solutions for which eq. (10) holds were called "ideal solutions" by M. J. Buerger (1933) and "optically ideal solutions" by several following workers (Butler, 1933; Kaiser and Parrish 1939; Darneal, 1948). To the extent that the molar volumes of the components are equal, v_i equals N_i and therefore eq. (10) becomes

$$n = \sum n_i N_i$$

which, expressed for just two components, is identical with eq. (8).

The derivation of eq. (10) assumes: (1) No interaction between the components of the solution occurs; (2) The volume of the solution is equal to the sum of the volumes of its components prior to mixing; (3) Normal incidence of light. The system being studied, since (for it) volume is not quite additive, is therefore not expected to conform to a linear relationship such as eq. (10).

In addition to the Mallard equations (Eqs. 8 and 9), the following equations relating refractive index (and density) to composition were tested with respect to the system studied. The Gladstone-Dale equation:

$$\frac{n-1}{\rho} = \frac{(n_a-1)w_a}{\rho_a} + \frac{(n_b-1)w_b}{\rho_b} + \dots \quad (11)$$

The Lorentz-Lorenz equation:

$$\frac{n^2-1}{(n^2+2)\rho} = \frac{(n_a^2-1)w_a}{(n_a^2+2)\rho_a} + \frac{(n_b^2-1)w_b}{(n_b^2+2)\rho_b} + \dots \quad (12)$$

The Lichtenecker equation:

$$\frac{\log n}{\rho} = \frac{(\log n_a)w_a}{\rho_a} + \frac{(\log n_b)w_b}{\rho_b} + \dots \quad (13)$$

The Newton-Drude equation:

$$\frac{n^2-1}{\rho} = \frac{(n_a^2-1)w_a}{\rho_a} + \frac{(n_b^2-1)w_b}{\rho_b} + \dots \quad (14)$$

And the equation introduced by Allen (1956):

$$\frac{n^3}{\rho} = \frac{n_a^3 w_a}{\rho_a} + \frac{n_b^3 w_b}{\rho_b} + \dots \quad (15)$$

Thus, assuming that ρ , the density of a solution is known, then n , the solution's refractive index can be calculated from the refractive indices, densities, and weight fractions of its components (*e.g.* $N_a, \rho_a, w_a; N_b, \rho_b, w_b$; etc.) on the basis of the foregoing equations. If this is done for solutions 2-7, the calculated indices (Table 5) are closest to those measured if the Lorentz-Lorenz relationship is used, slightly more variant for the Lichtenecker equation, and increasingly variant for the Gladstone-Dale, Newton-Drude, and Allen equations. Both Mallard equations proved least satisfactory of all, yielding such erroneous results that they were not tabulated.

If ideal solutions are being dealt with, equation (d) in Table 2 applies. Thus this value for weight fraction may be substituted into eqs. (11)-(15) to eliminate the density terms. The resultant equations, now compositionally expressed in terms of volume fractions (*i.e.* v_a, v_b , etc.), are:

$$n-1 = (n_a-1)v_a + (n_b-1)v_b + \dots$$

or

$$n = n_a v_a + n_b v_b + \dots ; \tag{16}$$

$$\frac{n^2 - 1}{n^2 + 2} = \frac{(n_a^2 - 1)v_a}{n_a^2 + 2} + \frac{(n_b^2 - 1)v_b}{n_b^2 + 2} + \dots ; \tag{17}$$

$$\log n = v_a \log n_a + v_b \log n_b + \dots ; \tag{18}$$

$$n^2 - 1 = (n_a^2 - 1)v_a + (n_b^2 - 1)v_b + \dots$$

TABLE 5. CALCULATION OF REFRACTIVE INDEX FROM DENSITY

No.	n _{exp.}	Refractive index calculated from the following equations:					p _{exp.}
		Lorentz-Lorenz	Lichte-necker	Gladstone-Dale	Newton-Drude	Allen	
15° C.	2 1.6467	1.6475	1.6477	1.6494	1.6508	1.6511	1.5668
	3 1.6617	1.6647	1.6649	1.6672	1.6691	1.6698	1.9377
	4 1.6776	1.6808	1.6810	1.6834	1.6853	1.6861	2.2522
	5 1.6912	1.6949	1.6952	1.6974	1.7027	1.6999	2.5235
	6 1.7074	1.7091	1.7094	1.7112	1.7127	1.7133	2.7877
	7 1.7232	1.7238	1.7240	1.7251	1.7261	1.7262	3.0401
	20° C.	2 1.6444	1.6449	1.6450	1.6468	1.6482	1.6485
3 1.6589		1.6616	1.6619	1.6642	1.6661	1.6667	1.9304
4 1.6744		1.6776	1.6789	1.6803	1.6821	1.6829	2.2240
5 1.6874		1.6914	1.6917	1.6939	1.6957	1.6964	2.5136
6 1.7034		1.7056	1.7069	1.7077	1.7093	1.7098	2.7773
7 1.7188		1.7201	1.7203	1.7215	1.7225	1.7228	3.0287
22° C.		2 1.6432	1.6439	1.6440	1.6458	1.6472	1.6487
	3 1.6572	1.6603	1.6606	1.6630	1.6648	1.6655	1.9277
	4 1.6728	1.6763	1.6766	1.6789	1.6808	1.6815	2.2408
	5 1.6864	1.6898	1.6901	1.6923	1.6942	1.6948	2.5097
	6 1.7018	1.7040	1.7044	1.7061	1.7076	1.7081	2.7733
	7 1.7166	1.7183	1.7174	1.7197	1.7206	1.7210	3.0240
	25° C.	2 1.6418	1.6423	1.6424	1.6442	1.6456	1.6460
3 1.6558		1.6586	1.6588	1.6612	1.6637	1.6638	1.9234
4 1.6705		1.6744	1.6746	1.6770	1.6789	1.6797	2.2358
5 1.6839		1.6879	1.6881	1.6904	1.6922	1.6928	2.5044
6 1.6998		1.7017	1.7020	1.7039	1.7054	1.7061	2.7666
7 1.7140		1.7160	1.7162	1.7174	1.7184	1.7189	3.0172
30° C.		2 1.6392	1.6400	1.6400	1.6418	1.6432	1.6435
	3 1.6529	1.6560	1.6560	1.6585	1.6604	1.6609	1.9162
	4 1.6668	1.6710	1.6710	1.6736	1.6755	1.6761	2.2261
	5 1.6806	1.6844	1.6844	1.6869	1.6887	1.6893	2.4939
	6 1.6962	1.6980	1.8989	1.7001	1.7016	1.7020	2.7549
	7 1.7098	1.7122	1.7120	1.7135	1.7144	1.7149	3.0048

or

$$n^2 = n_a^2 v_a + n_b^2 v_b + \dots; \quad (19)$$

$$n^3 = n_a^3 v_a + n_b^3 v_b + \dots \quad (20)$$

These equations, applied to solutions 2-7 in the same manner as were eqs. (11)-(15), yield even less accurate results, possibly because of the non-ideality of these solutions.

Equations (11)-(20) could well be applied to solid solutions, equations (16)-(20) applying to the extent that the solid solution series approaches ideality. On the basis of the present results for diiodomethane- α -monochloronaphthalene solutions, the refractive indices of solid solutions should be calculable to within 4% of the index difference between the "end members" if the Lorentz-Lorenz equation is used.

EFFECT OF TEMPERATURE ON REFRACTIVE INDEX

For a given material, according to the theoretical discussion of Mott and Gurney (1950), the value of $(n^2-1)/(n^2+2)$ varies linearly with temperature. The data for solutions 1-8 appear to corroborate this, differing but little from the linear regression lines obtained by a least squares analysis of the data (Fig. 4).¹ The Mott-Gurney relation may be restated as

$$\frac{(n^2 - 1)}{(n^2 + 2)} = Pt \quad (21a)$$

where P , a constant, here indicates the slope of the line obtained if $(n^2-1)/(n^2+2)$ is plotted against temperature t for a given substance. Taking the derivative with respect to t of both sides of Eq. (21a) we obtain

$$\frac{6n}{(n^2 + 2)^2} \frac{dn}{dt} = P \quad (21b)$$

from which we see that

$$\frac{dn}{dt} = \frac{(n^2 + 2)^2}{6n} P \quad (21c)$$

Since the slope P is always negative, so is dn/dt .

For each solution, (1) to (8), the slope P for the line relating $(n^2-1)/(n^2+2)$ to temperature t was obtained by a least squares analysis of the observed data. Substitution of P into eq. (21c) then permitted dn/dt to be calculated for each temperature of measurement. For each solution, dn/dt decreased slightly in value as temperature in-

¹ Butler's (1933) data on indices of refraction of kerosene and α -monochloronaphthalene solutions further substantiate the Mott-Gurney discussion.

TABLE 6. VALUES OF $-P$, $-(dn/dt)$, AND γ FOR THE SOLUTIONS STUDIED

Sample	$-P$	$-(dn/dt) \times 10^4$						$\gamma \times 10^4$ ¹
	15°-30° C.	15° C.	20° C.	22° C.	25° C.	30° C.	av.	15°-30° C.
1	1.88×10^{-4}	4.19	4.18	4.18	4.17	4.16	4.2	2.56
2	2.28×10^{-4}	5.12	5.11	5.11	5.10	5.09	5.1	3.11
3	2.61×10^{-4}	5.93	5.92	5.91	5.91	5.89	5.9	3.57
4	3.61×10^{-4}	7.28	7.26	7.25	7.24	7.21	7.3	4.34
5	3.00×10^{-4}	6.98	6.96	6.96	6.94	6.92	6.9	4.13
6	3.50×10^{-4}	8.25	8.23	8.22	8.20	8.18	8.2	4.83
7	3.54×10^{-4}	8.46	8.43	8.41	8.39	8.36	8.4	4.90
8	3.36×10^{-4}	8.15	8.12	8.11	8.10	8.07	8.1	4.67

¹ Taken to be the slope of the plot of $\ln n$ vs. temperature for each solution. This assumes that γ is relatively independent of temperature in the range between 15° and 30°.

creased, particularly for the diiodomethane-rich solutions (Table 6). Thus, strictly speaking, dn/dt is not independent of temperature.

The writers also calculated what will be called the "thermal coefficient of refraction" (γ) for each solution, this being defined as

$$\gamma = -\frac{1}{n} \frac{dn}{dt} \quad (22)$$

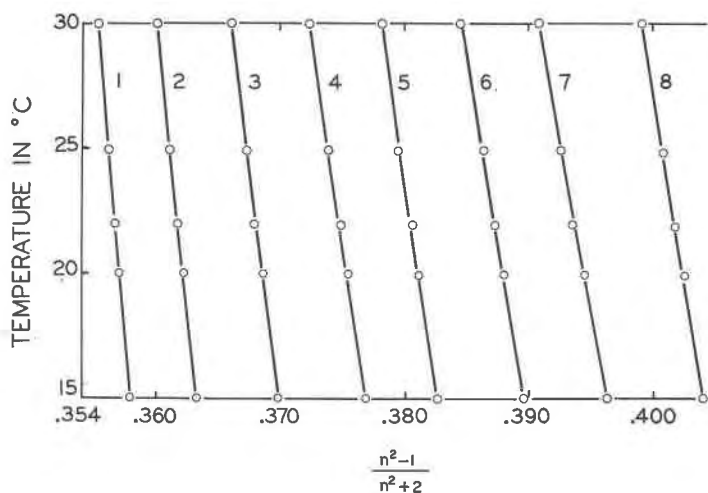


FIG. 4. Variation of $(n^2-1)/(n^2+2)$ with respect to temperature for solutions (1) to (8) of the α -monochloronaphthalene-diiodomethane series.

However, for a given temperature, neither γ , dn/dt , or P varied linearly with composition for the α -monochloronaphthalene-diiodomethane series studied.

Buerger (1933) considered dn/dt and n to be linearly related for "optically ideal, binary solutions," *i.e.*

$$\frac{dn}{dt} = kn$$

or

$$\frac{1}{n} \frac{dn}{dt} = k$$

where k is a constant, *i.e.*, is possessed of the same value for all end members of the series. From eq. (22) it is obvious that $k = -\gamma$; hence dn/dt is linearly related to n only if the end members possess equal thermal coefficients of refraction. In this latter case the slope of the straight line relating dn/dt and n yields the thermal coefficient of refraction for either member.

In such a solution series it is also unlikely that dn/dt will vary linearly with volume fraction, *i.e.*

$$\frac{dn}{dt} = \sum \frac{dn_i}{dt} v_i. \quad (23)$$

For this to hold, it is necessary that eq. (10) also hold for the series (which is in itself doubtful). Differentiation of eq. (10) with respect to temperature yields

$$\frac{dn}{dt} = \sum \frac{dn_i}{dt} v_i + \sum n_i \frac{dv_i}{dt}. \quad (24)$$

The second term on the right side of eq. (24) must equal zero, if eqs. (23) and (24) are to become identical. Such is the case only if volume per cent is unchanged by temperature, *i.e.* $dv_i/dt = 0$. This, of course, only pertains if the thermal coefficients of expansion of all members of the system are equal (*cf.* eq. (6b)). Thus eq. (23) is expected to hold only under very limiting circumstances.

DENSITY AND REFRACTIVE INDEX RELATIONSHIPS

Ritland (1955) observed a linear relationship between density and refractive index for a borosilicate glass treated at various temperatures, and concluded that its refractive index was a simple function of its density as temperature was varied. A similar relationship exists for individual solutions in the system α -monochloronaphthalene-diiodomethane studied here. Thus density appears to be a simple function of refractive

index for these materials, *i.e.*

$$\left(\frac{\partial \rho}{\partial n}\right)_c = \xi \quad (25)$$

where ξ equals a constant and c refers to composition.

In contrast, the relation between density and refractive index¹ for a series of solutions of differing compositions (but at a constant temperature) is likely to be non-linear in the ultimate analysis. In other words, $(\partial n / \partial \rho)_t$ is not likely to equal a constant for such a solutional series. To determine the conditions necessary for $(\partial n / \partial \rho)_t$ to equal a constant, assume that density and refractive index of solutions in the series are both functions of temperature and composition, thus

$$\rho = \rho(c, t) \quad (26)$$

$$n = n(c, t). \quad (27)$$

Consequently

$$\left(\frac{\partial \rho}{\partial n}\right)_c = \frac{\left(\frac{\partial \rho}{\partial t}\right)_c}{\left(\frac{\partial n}{\partial t}\right)_c} \quad (28)$$

and

$$\left(\frac{\partial \rho}{\partial n}\right)_t = \frac{\left(\frac{\partial \rho}{\partial c}\right)_t}{\left(\frac{\partial n}{\partial c}\right)_t}. \quad (29)$$

If ρ and n have a linear relation to each other, the Jacobian determinant of eqs. (28) and (29) should vanish (*cf.* Bronwell, 1955), *i.e.*

$$\frac{\partial(\rho, n)}{\partial(c, t)} = \begin{vmatrix} \left(\frac{\partial \rho}{\partial c}\right)_t & \left(\frac{\partial \rho}{\partial t}\right)_c \\ \left(\frac{\partial n}{\partial c}\right)_t & \left(\frac{\partial n}{\partial t}\right)_c \end{vmatrix} = 0. \quad (30)$$

Combining eqs. (28), (29), and (30) we obtain

$$\frac{\left(\frac{\partial \rho}{\partial n}\right)_t}{\left(\frac{\partial \rho}{\partial n}\right)_c} = 1 \quad (31)$$

as the condition which must be fulfilled if the relation between n and ρ for a solutional series is to be truly linear.

If n is plotted on the abscissa and ρ on the ordinate, the isothermal

¹ For a given wavelength of monochromatic light.

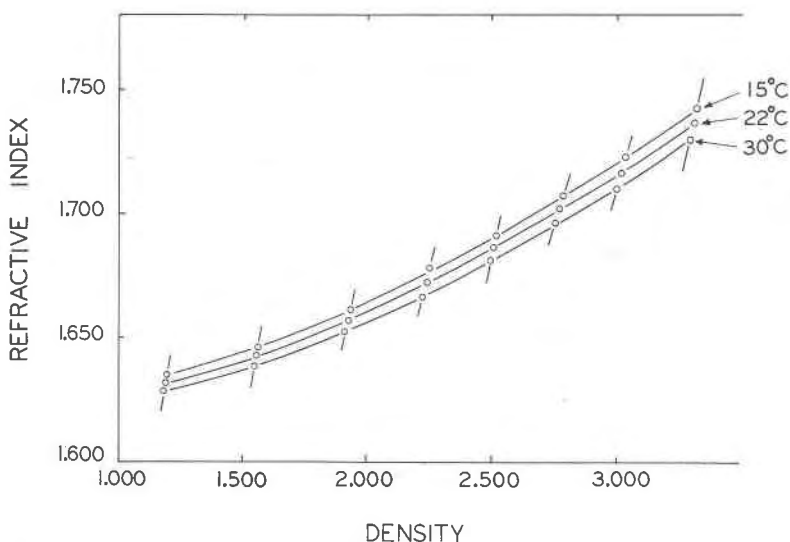


FIG. 5. Relation between refractive index and density for solutions of the α -monochloronaphthalene-diiodomethane series at temperatures 15°, 22°, and 30°. These same curves, on a graph paper background, are also presented by Bloss (1961, p. 64).

curve relating refractive index and density for a solution series will be convex upward, truly linear, or concave upward according to the extent that the ratio in eq. (31) exceeds, equals, or is less than 1.0, respectively. For the solutions studied the ratio exceeds 1.0 and a convex upward curve results (Fig. 5).

The α -monochloronaphthalene-diiodomethane media of other laboratories can easily be adapted for use as a graded series of density standards for sink-float tests of small grains. Assuming n_D is known to within 0.001, density can be determined to within 0.03 for the less dense and to within 0.01 for the more dense liquids of these sets of immersion media. To do this use either Fig. 5 or, better yet, similar graphs of the data of Table 1 made to a much larger scale.

Extrapolation of these data to media in other laboratories should occasion no serious errors since samples of diiodomethane and of α -monochloronaphthalene from other laboratories agreed in refractive index and density (within the limits of experimental error) with those reported here. Although a purchase date span of five years was involved, agreement was exceedingly good between diiodomethane samples. A five year old sample of α -monochloronaphthalene possessed a density which was .0021 lower than our sample, this being the only result which was beyond the limits of experimental error. Blends from older stocks such as those

used by Kaiser and Parrish (1939) might occasion greater inaccuracies if Fig. 5 is applied to them.

A truly linear relation between refractive index and density for a series of solutions requires such special conditions that it is likely to be the exception rather than the rule. The data for Clérici solution (Jahns, 1939) at first sight indicate a linear relation for 21° C. However, if this linear isotherm is extended, it does not pass through the point indicating the refractive index and density of water at 21° C. Thus a slightly non-linear relation between refractive index and density is suspected for Clérici solution.

In the search for a miscible series for which the relation between ρ and n is linear, $(\partial\rho/\partial n)_c$ should be equal in value for both end members. From eq. (28), the value $(\partial\rho/\partial n)_c$ may be calculated if the right hand terms are known. Commonly, however, only dn/dt , but not $d\rho/dt$, is cited for immersion media. The latter value must thus be measured.

The "ideal solutions" discussed by M. J. Bueger (1933) and "optically ideal solutions" discussed by others (Butler, 1933; Kaiser and Parrish, 1939; Darneal, 1948) were defined as binary solutions for which refractive index was linearly related to volume fraction, *i.e.*, for which

$$n = \sum n_i v_i \quad (10)$$

or, stated alternatively, for which

$$\left(\frac{\partial n}{\partial c}\right)_t = k_1 \quad (32)$$

where k_1 is a constant. Continuing our assumption that n and ρ are functions of composition, c ,

$$\frac{\left(\frac{\partial \rho}{\partial c}\right)_t}{\left(\frac{\partial n}{\partial c}\right)_t} = \left(\frac{\partial \rho}{\partial n}\right)_t \quad (33)$$

For "optically ideal solutions" therefore,

$$\frac{\left(\frac{\partial \rho}{\partial c}\right)_t}{\left(\frac{\partial n}{\partial c}\right)_t} = k_1 \quad (34)$$

For an ideal system $(\partial\rho/\partial c)_t$ equals a constant if c is expressed in volume fractions (Fujii, 1960). Thus, for a thermodynamically ideal solution to be "optically ideal" as well,

$$\left(\frac{\partial \rho}{\partial n}\right) = \frac{\left(\frac{\partial \rho}{\partial c}\right)_t}{k_1} = k_2 \quad (35)$$

where k_2 is also a constant. Consequently, solution series for which density and refractive index are linearly related may be concluded to be "optically ideal" and vice versa.

DISPERSION

The refractive indices of the liquids studied were measured at wavelengths, (Hg) 4358, 5461, and 5780 Å (± 10 Å) (Table 7), and at (Na) 5893 Å. For each liquid these data were plotted on Hartman dispersion nets to yield straight lines for each temperature studied (15.0, 20.0, 22.0, 25.0, and 30.0° C.). From these lines, indices n_F and n_C were determined (Table 8) and the common measurements of dispersion ($n_F - n_C$) and

$$\left(\frac{n_D - 1}{n_F - n_C} \right)$$

could be determined for each liquid (and temperature). For each liquid the average value of ($n_F - n_C$) and of

$$\left(\frac{n_D - 1}{n_F - n_C} \right)$$

for the five temperatures investigated was computed. For the solutions studied neither ($n_F - n_C$) nor

$$\left(\frac{n_D - 1}{n_F - n_C} \right)$$

was linearly related to volume fraction (Fig. 6).

Considering solution series in general, ($n_F - n_C$) can be expected to be linearly related to volume fraction only if refractive index is so related. Differentiating the Cauchy equation (*cf.* Jenkins and White, 1957, p. 468)

$$n = n_0 + \frac{A}{\lambda^2} \tag{36}$$

with respect to composition we obtain

$$\left(\frac{\partial n}{\partial c} \right)_t = \left(\frac{\partial n_0}{\partial c} \right)_t + \frac{1}{\lambda^2} \left(\frac{\partial A}{\partial c} \right)_t \tag{37}$$

From this we can see that if $(\partial n / \partial c)_t$ equals a constant, so must $(\partial n_0 / \partial c)_t$. Consequently $(\partial A / \partial c)_t$ must also equal a constant. From the Cauchy equation, however, we obtain

$$n_F - n_C = A \frac{\lambda_C^2 - \lambda_F^2}{\lambda_C^2 \lambda_F^2} \tag{38}$$

and, since

$$\frac{\lambda_C^2 - \lambda_F^2}{\lambda_C^2 \lambda_F^2}$$

TABLE 7. REFRACTIVE INDEX AT VARIOUS WAVE LENGTHS FOR α -MONOCHLORONAPHTHALENE-DIODOMETHANE SOLUTIONS

Sample	15.0±0.1° C.		20.0±0.1° C.		22.0±0.1° C.		25.0±0.1° C.		30.0±0.1° C.			
	Hg 4359	Hg 5461	Hg 5780	Hg 4359	Hg 5461	Hg 5780	Hg 4359	Hg 5461	Hg 5780	Hg 4359	Hg 5461	Hg 5780
1	1.6723	1.6420	1.6364	1.6699	1.6392	1.6340	1.6688	1.6387	1.6335	1.6672	1.6371	1.6318
2	1.6857	1.6541	1.6483	1.6832	1.6514	1.6440	1.6822	1.6504	1.6450	1.6801	1.6490	1.6437
3	1.7022	1.6697	1.6640	1.6991	1.6671	1.6612	1.6982	1.6651	1.6592	1.6947	1.6635	1.6576
4	1.7187	1.6853	1.6795	1.7146	1.6817	1.6757	1.7134	1.6801	1.6742	1.7116	1.6784	1.6726
5	1.7332	1.6988	1.6928	1.7302	1.6954	1.6891	1.7286	1.6944	1.6885	1.7262	1.6921	1.6860
6	1.7516	1.7161	1.7100	1.7476	1.7120	1.7051	1.7454	1.7102	1.7040	1.7436	1.7090	1.7024
7	1.7677	1.7313	1.7250	1.7649	1.7278	1.7213	1.7606	1.7252	1.7186	1.7576	1.7225	1.7160
8	1.7892	1.7516	1.7448	1.7857	1.7476	1.7408	1.7834	1.7458	1.7393	1.7812	1.7432	1.7364

The magnitude of error is same as those of Table 1.

TABLE 8. VALUES OF n_F , n_C , $(n_F - n_C)$, AND $(n_D - 1)/(n_F - n_C)$ FOR THE SOLUTIONS STUDIED¹

Sample	n_F						n_C						$n_F - n_C$		$n_D - 1$ $n_F - n_C$				
	15° C.	20° C.	22° C.	25° C.	30° C.	30° C.	15° C.	20° C.	22° C.	25° C.	30° C.	30° C.	15° C.	20° C.	22° C.	25° C.	30° C.	ave. 15°-30° C.	ave. 15°-30° C.
1	1.6556	1.6533	1.6523	1.6504	1.6486	1.6486	1.6260	1.6237	1.6230	1.6216	1.6198	1.6198	0.0296	0.0296	0.0293	0.0288	0.0288	0.0292 ²	2.163
2	1.6682	1.6656	1.6648	1.6628	1.6604	1.6604	1.6379	1.6352	1.6346	1.6332	1.6303	1.6303	0.0303	0.0304	0.0302	0.0296	0.0301	0.0301	2.135
3	1.6844	1.6818	1.6800	1.6778	1.6754	1.6754	1.6530	1.6501	1.6482	1.6470	1.6444	1.6444	0.0314	0.0317	0.0318	0.0308	0.0324	0.0313	2.098
4	1.7004	1.6964	1.6950	1.6932	1.6904	1.6904	1.6683	1.6642	1.6625	1.6610	1.6580	1.6580	0.0321	0.0322	0.0325	0.0322	0.0324	0.0323	2.091
5	1.7144	1.7110	1.7100	1.7073	1.7036	1.7036	1.6812	1.6774	1.6762	1.6742	1.6712	1.6712	0.0332	0.0336	0.0338	0.0331	0.0324	0.0332	2.065
6	1.7321	1.7279	1.7258	1.7244	1.7212	1.7212	1.6980	1.6932	1.6918	1.6908	1.6872	1.6872	0.0341	0.0347	0.0340	0.0336	0.0340	0.0341	2.059
7	1.7479	1.7431	1.7409	1.7381	1.7338	1.7338	1.7136	1.7092	1.7070	1.7042	1.7002	1.7002	0.0343	0.0339	0.0339	0.0339	0.0336	0.0339	2.083
8	1.7689 ³	1.7647	1.7628	1.7601	1.7562	1.7562	1.7317 ³	1.7282	1.7266	1.7237	1.7201	1.7201	0.0372	0.0365	0.0362	0.0364	0.0361	0.0368 ³	2.018

¹ The values for n_F and n_C were obtained graphically from empirically determined dispersion curves.

² Ermons and Gates (1944) give $(n_F - n_C)$ at 24° C. as 0.030 and 0.0369 for α -monochloronaphthalene and diiodomethane, respectively.

³ Timmerman (1950) gives n_F and n_C for diiodomethane at 15° C. as 1.77161 and 1.73403.

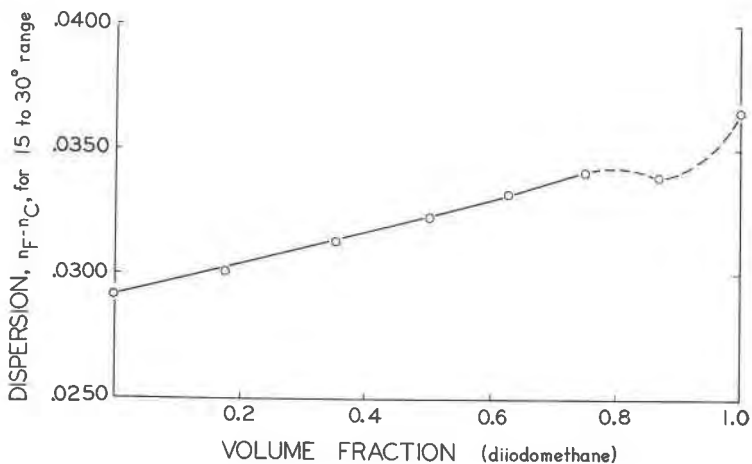


FIG. 6. Variation of the dispersion, $(n_F - n_C)$, with respect to volume fractions of diiodomethane for solutions of the α -monochloronaphthalene-diiodomethane system.

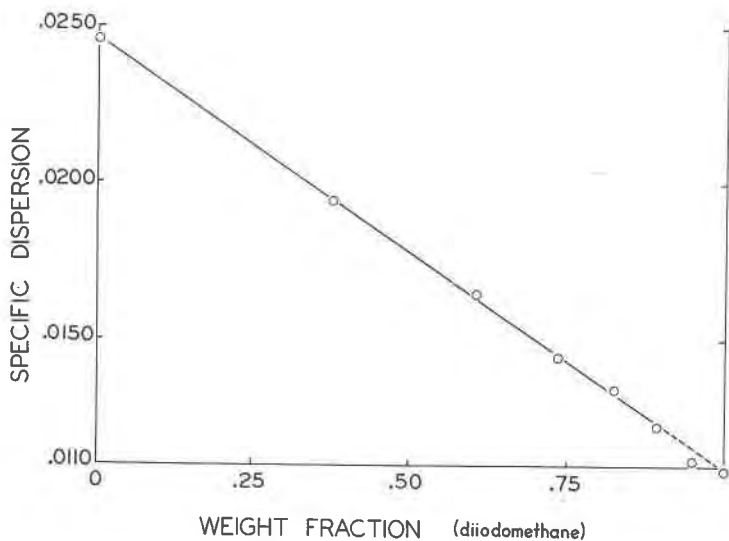


FIG. 7. Variation of the specific dispersion $(n_F - n_C)/\rho$, with respect to weight fractions of diiodomethane for solutions of the α -monochloronaphthalene-diiodomethane system.

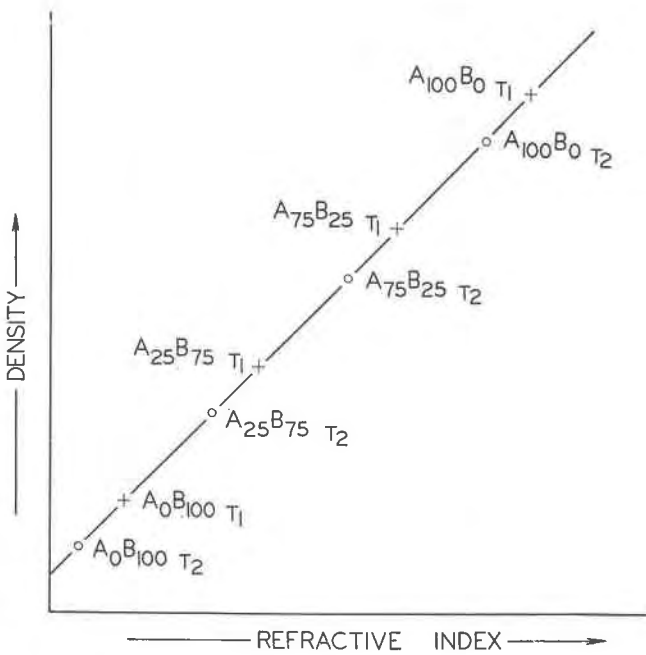


FIG. 8. Illustration of a precisely linear relation between density and composition for a solution series between A and B. Note that the line expressing this relation is independent of temperature. For example, regardless of whether a solution is measured at t_1 , t_2 , or some other temperature, the plot of its density against refractive index falls on this same line. (This illustration is thus a graphic statement of the equality

$$\left(\frac{\partial \rho}{\partial n}\right)_c = \left(\frac{\partial \rho}{\partial n}\right)_t.$$

is a constant,

$$\left(\frac{\partial(n_F - n_C)}{\partial c}\right)_t$$

must also equal a constant.

Grosse and Wachner (1939) linearly correlated dispersion with composition in weight fraction for a binary system by using specific dispersion (δ), which they defined for a particular temperature, as

$$\delta = \frac{n_F - n_C}{\rho}. \quad (39)$$

This relationship, obtained empirically by them, is actually a necessary corollary of the Gladstone-Dale equation. Applying this latter equation to the two wavelengths involved,

$$\frac{n_F - 1}{\rho} = K_F \quad \text{and} \quad \frac{n_C - 1}{\rho} = K_C$$

TABLE 9. SPECIFIC DISPERSION, δ , FOR THE SOLUTIONS STUDIED

	15°	20°	22°	25°	30°
1	0.0247	0.0248	0.0246	0.0242	0.0243
2	0.0193	0.0195	0.0194	0.0190	0.0194
3	0.0162	0.0164	0.0165	0.0160	0.0169
4	0.0143	0.0143	0.0145	0.0144	0.0146
5	0.0132	0.0134	0.0135	0.0132	0.0136
6	0.0122	0.0125	0.0123	0.0121	0.0123
7	0.0113	0.0112	0.0112	0.0112	0.0112
8	0.0112	0.0110	0.0109	0.0110	0.0110

whereupon it is obvious that

$$\delta = K_F - K_C. \quad (40)$$

To the extent that the Gladstone-Dale equation is applicable to a system, then specific dispersion may also be linearly correlated with the composition of the system (in weight fractions). This is approximately true for the system studied (Fig. 7 and Table 9).

CONCLUSIONS

A. For α -monochloronaphthalene-diiodomethane immersion media:

1. Volume is not an additive property of the system. Thus the system is thermodynamically non-ideal.
2. Non-ideality is further substantiated by the observed non-linear relationship between volume fractions and the coefficients of thermal expansion for the series.
3. Density and refractive index are not linearly related (*cf.* Fig. 5).
4. If of recent American manufacture, these media may be used to measure the densities of small grains by the sink-float method with an accuracy of 0.01 to 0.03, the greater accuracy being applicable to the denser members of the series.
5. Dispersion $(n_F - n_C)$ is not linearly related to volume fractions whereas specific dispersion $(n_F - n_C)/\rho$ is approximately linearly related to weight fractions.
6. The observed relations between density, refractive index, and composition in weight fractions is closest to the Lorentz-Lorenz relation (eq. 12), almost as close for the Lichtenecker relation (eq. 13), but increasingly variant for the Gladstone-Dale, Newton-Drude, and Allen equations.

B. For solutional series in general:

7. The isothermal curves relating density and refractive index are not likely to be straight lines, that is, $(\partial\rho/\partial n)_t$ is not likely to equal a constant.
8. For such a linear relationship to exist, $(\partial\rho/\partial n)_c$ must be equal for all end members, that is $(\partial\rho/\partial n)_c$ must equal a constant for the series.
9. In the event of such linearity, the equation

$$\left(\frac{\partial\rho}{\partial n}\right)_c = \left(\frac{\partial\rho}{\partial n}\right) \quad (33)$$

must hold for the series. Illustrated graphically this equality means, for example, that the points in Fig. 8 will be collinear even though these four solutions were measured at two different temperatures, t_1 and t_2 . Thus a truly linear relation between density and refractive index will be independent of temperature.

10. A non-linear relation between refractive index and density will not be independent of temperature. Fig. 5, for example, shows that the 15°, 22°, and 30° C. isotherms relating density and refractive index do not coincide for the system studied (as they would have if the relation was truly linear).
11. "Optically ideal" solutional series, by definition those in which refractive index and composition in volume fractions are linearly related, represent a rather specialized class of (thermodynamically) ideal solutions to which the conditions stated in conclusion (9) must also apply.

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