Refractive Index–Density Slope Associated with Volume Change on Mixing

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Refractive index and density data for aqueous blends of 21 organic compounds were studied in relation to ideal volume % composition. The effect of deviation from ideality (volume change on mixing) was studied from the point of view of the slope $\Delta n/\Delta d$ for the tie line connecting the observed point on a plot of n vs. d with the n_L and d_L points calculated by linear interpolation—i.e., the ideal point for no volume change on mixing. This study leads to the hypothesis that when hydrogen bonding is low, the Sellmeier-Drude (or Newton) specific refraction, $(n^2 - 1)/d = C$, represents the relation between n and d when there is volume change on mixing. The deviation from linearity relative to ideal volume % composition is also studied for a number of functions of n and d which have been used for analytical purposes. The Newton function is best for the aqueous solutions of glycols, ethers, and amines presented in this paper, and the Gladstone-Dale function is best for solutions of acetone and methyl alcohol in water.

FOR solutions of acetone in water, there is about 4.1% maximum volume decrease at 20° C. (*18*). The change of refractive index and density relative to the properties of the hypothetical ideal mixture (no volume change on mixing) are shown to be represented by the Gladstone and Dale specific refraction relation (*8*) with an accuracy of about 0.0002 in refractive index [Table VI (*18*)]. The Gladstone and Dale specific refraction equation is

$$(n - 1)/d = \text{constant} \qquad (1)$$

from which one can deduce that

$$\Delta n/\Delta d = (n_L - 1)/d_L \qquad (2)$$

In Equation 2, the subscript L signifies the properties of a blend assuming no volume change on mixing. Such properties are calculated by linear interpolation on the ideal volume % basis (*11, 13, 15, 23, 28, 29*).

For the acetone-water blends over a wide range of concentrations, the slope calculated with Equation 2 agrees with the slope calculated from the experimental data, on the average for 25 acetone blends within 1% [column H, Table V (*18*)].

Since the graphic slope $\Delta n/\Delta d$ is different (*18*) for each of the well known specific refraction (*11, 15-17*) equations, it is pertinent to tabulate this slope associated with volume change on mixing. The objective is to see how other binary aqueous mixtures compare with the acetone water blends referred to previously (*18*), and to find out if the majority of aqueous binary solvent blends follow any one specific refraction relation.

This paper will consider primarily the binary blends previously studied by Thompson and others (*2-5, 7, 21, 22, 25, 32*). Table I shows data for aqueous blends of ethylene glycol monomethyl ether calculated using Equation 2. The slope $\Delta n/\Delta d$ (column F, Table I) is about 10 to 15% too great (column H, Table I). In terms of refractive index, this means that the calculated refractive index obtained by applying the Gladstone-Dale function is too high by about 10 units in the fourth decimal place (column I, Table I).

Table I. Comparison of Calculated and Observed $\Delta n/\Delta d$ for Blends of Water and Ethylene Glycol Monomethyl Ether Using Gladstone and Dale Specific Refraction, 25° C.

Vol. % Organic A	d_L B	d/d_L C	% Vol. Decrease D	n_L E	$\Delta n/\Delta d$, Calcd.[a] F	$\Delta n/\Delta d$, Obs. G	Ratio, F/G H	Obs. n − Calcd. $n \times 10^4$ I
10.38	0.9933	1.0061	0.61	1.3395	0.3418	0.281	1.215	−4
21.07	0.9893	1.0135	1.3	1.3468	0.3506	0.276	1.270	−9
30.88	0.9857	1.0201	2.0	1.3534	0.3585	0.308	1.164	−10
40.99	0.9820	1.0255	2.5	1.3602	0.3668	0.324	1.132	−10
50.98	0.9783	1.0286	2.8	1.3670	0.3751	0.329	1.140	−13
61.08	0.9753	1.0281	2.7	1.3739	0.3834	0.347	1.105	−10
71.14	0.9709	1.0253	2.5	1.3807	0.3921	0.354	1.108	−9
80.63	0.9674	1.0200	2.0	1.3871	0.4001	0.351	1.140	−9
90.52	0.9638	1.0110	1.1	1.3938	0.4086	0.368	1.135	−4
						Average	1.154	−8.7

[a] Calculated using Equation 2.

Table II. Comparison of Calculated and Observed $\Delta n/\Delta d$ for Blends of Water and Ethylene Glycol Monomethyl Ether (*4*) Using Newton Specific Refraction, 25° C.

Vol. % Organic A	$\frac{n_L^2 - 1}{d_L}$ B	n^a, Calcd. C	$\Delta n/\Delta d$,[b] Calcd. D	$\Delta n/\Delta d$, Obs. E	D/E	Obs. n − Calcd. $n \times 10^4$
10.38	0.7996	1.3413	0.298	0.281	1.059	−1
21.07	0.8227	1.3508	0.305	0.276	1.081	−3
30.88	0.8438	1.3596	0.311	0.308	1.016	−1
40.99	0.8657	1.3681	0.317	0.324	0.975	+2
50.98	0.8880	1.3761	0.324	0.329	0.989	+1
61.08	0.9101	1.3829	0.330	0.347	0.947	+5
71.14	0.9335	1.3890	0.337	0.354	0.954	+4
80.63	0.9552	1.3937	0.343	0.351	0.971	+2
90.52	0.9781	1.3975	0.349	0.368	0.949	+2
			Average		0.993	3

[a] n calculated with Newton specific refraction equation. [b] Δn calculated from known Δd and values of d_L and n_L, using Equation 3, by substitution of the appropriate values and solving for n.

Table II shows that for these data the slope $\Delta n/\Delta d$ (column D, Table II) calculated with the Newton function

$$\frac{n^2 - 1}{d} = c_1 \tag{3}$$

agrees with the observed graphic slope (column E, Table II) within a few per cent. [The observed slope is the same as the slope of the tie lines in Figure 2 (*18*)]. In terms of refractive index, the agreement is about 1 to 3 units in the fourth decimal.

Since the other refraction functions, namely the Eykman function (*6, 18*) and the Lorentz-Lorenz (*18-20*) functions, would give steeper slopes than the Gladstone-Dale function (*8, 16*), these were not calculated for ethylene glycol monomethyl ether.

In comparing other solutions, only the slopes corresponding to the Gladstone-Dale and the Newton functions were calculated. Since the slopes in the middle concentration ranges are very consistent, [Table V, (*18*), Tables I and II this paper] only the concentration nearest 50% was used for the other blends.

Table III presents data for 21 blends of organic liquids in water. Data are given for the properties of the pure liquids, and the composition and properties of the blend nearest 50% for which data are available. Derived values shown are the ideal density and refractive index calculated from the volume % composition, the observed value of $\Delta n/\Delta d$ corresponding to the volume change on mixing, and the value of this slope obtained when Δn was calculated from n, d, and Δd using either the Gladstone-Dale function (Equations 1 and 2), or the Newton function (Equation 3). The agreement of these calculated slopes with the experimental slopes is shown as ratios of calculated to observed. The agreement in terms of refractive index is also shown. All the data are for 25° C.

Acetic acid solutions show a very high slope, greater than that of the Gladstone and Dale function. The data indicate that solutions of acetone and hexylene glycol agree best with the Gladstone-Dale function. Methyl alcohol, isopropyl alcohol, and ethylene glycol monomethyl ether are intermediate between the Gladstone and Dale and the Newton function. The aqueous solutions for the other 15 compounds agree quite well with the Newton function (*11, 15-17*).

A preliminary hypothesis is that, when solution does not involve a change in the number or frequency of refracting electrons, the Sellmeier-Drude dispersion equation applies (*11, 15, 16, 17*). The Sellmeier-Drude dispersion equation is equivalent to the Newton specific refraction equation.

The Sellmeier-Drude dispersion equation can be written as follows for a pure compound.

$$\frac{n^2 - 1}{d} = \left(\frac{B^1}{V_0^2 - V^2}\right) \tag{4}$$

where

$$B^1 = \frac{kb}{M}\,\frac{Ae^2}{\pi m_0} \tag{5}$$

In these equations:

n = refractive index
d = density
V_0^2 = frequency of the dispersion electrons
V^2 = frequency of the light used
M = molecular weight
b = formula bonds per molecule
k = apparent dispersion electrons per formula bond
A = Avogadros constant
e = charge on an electron
m_0 = mass of an electron
π = 3.1416

For a solution, the values of n_L and d_L and the experimental values of n and d may be inserted in this equation. If for all the molecules concerned V_0, k, b, and M do not change as the density goes from d_L to the observed density, then the Newton function should apply, since the other terms in the equation are constant. If there is substantial hydrogen bonding, k, b, and M and possibly V_0 may be changed as density changes. This could account for the increase in slope for solutions of acetic acid, acetone and hexylene glycol and the intermediate slope values for methyl alcohol and isopropyl alcohol. Why normal propyl alcohol shows little of this effect is not clear.

It would seem worthwhile to study several of these solutions by obtaining refractive indices over a range of wave lengths and at more than one concentration. The apparent number and frequency of the dispersion electrons could then be calculated using Equations 4 and 5.

VOLUME CHANGE ON MIXING IN RELATION TO FREE VOLUME

The volume change on mixing was discussed in the first paper in this series from the point of view of the diminution of the free volume associated with molecules (*18*). Free volume in liquids has the properties of a perfect vacuum—i.e.; it is without weight and without refracting power (*11, 12*). For aqueous solutions such as studied in this paper, volume change on mixing diminishes this free volume (*11, 12, 14, 31*). In the absence of hydrogen bonding or chemical reaction, this change in free volume would not be expected to change the number or frequency of dispersion electrons in the molecules, but only the distance separating molecules.

The data for diethylenetriamine, triethylenetetramine, and tetraethylenepentamine are particularly interesting. This series of compounds can be represented by the formula

$$\mathrm{H\,(NHCH_2-CH_2)_n-NH_2}$$

where n = 2, 3, and 4 for the three compounds tested. This is essentially a repetitive series with a $-NH_2$ end group. The refractivity intercepts for these three compounds are nearly constant, which is as it should be for a repetitive series (*11, 15*).

This series also shows a relatively large contraction on mixing, namely, 5.0 to 5.1%. This amounts to 0.0514 cc. per gram for tetraethylenepentamine. The fact that one can calculate d_L and n_L; and then calculate refractive index using the Newton specific refraction, using n_L and Δd, and arrive

Table III. Comparison of $\Delta n/\Delta d$ for Volume Change on Mixing for Aqueous Solutions

Organic Component				Composition of Blends		Properties of Water Blends						Slope Ratio[b], Calcd./Obs.		Refractive Index Difference, Obs. – Calcd.		
	Properties															
Name	d_4^{25}	n_D^{25}	$n - d/2$	Vol. % org.	Wt. % org.	d_4^{25}	d_L	% Vol.[a] Decrease	n_D^{25}	n_L	$\Delta n/\Delta d$	$\Delta n/\Delta d$ G-D	$\Delta n/\Delta d$ Newton	$\Delta n \times 10^4$ G-D	$\Delta n \times 10^4$ Newton	Reference
Acetic acid[c]	1.0446	1.3698	0.8475	48.80	49.97	1.0532	1.0204	3.1	1.3638	1.3508	0.396	0.870	0.752	+17	+32	*30*
Acetone	0.7853	1.3559	0.9632	56.05	50.11	0.9167	0.8784	4.2	1.3606	1.3459	0.384	1.026	0.891	–4	+16	*18*
Methyl alcohol	0.7866	1.3265	0.9332	55.55	49.64	0.9130	0.8802	3.6	1.3408	1.3292	0.354	1.059	0.923	–7	+9	*5*
n-Propyl alcohol	0.7999	1.3833	0.9833	55.11	49.62	0.9063	0.8884	2.0	1.3670	1.3605	0.363	1.117	0.967	–8	+2	*5*
Isopropyl alcohol	0.7807	1.3749	0.9845	55.45	49.36	0.9039	0.8771	3.0	1.3662	1.3560	0.381	1.069	0.923	–7	+8	*5*
Hexylene glycol	0.9181	1.4257	0.9666	51.98	49.92	0.9851	0.9560	3.0	1.3921	1.3809	0.385	1.036	0.889	–4	+12	*2*
Dipropylene glycol	1.0165	1.4389	0.9306	49.20	49.69	1.0337	1.0066	2.6	1.3940	1.3848	0.339	1.122	0.966	–11	+3	*2*
Triethylene glycol	1.1195	1.4541	0.8943	46.80	49.69	1.0740	1.0544	1.8	1.3952	1.3894	0.296	1.241	1.071	–15	–4	*2*
Ethylene glycol monomethyl ether	0.9603	1.4002	0.9200	50.98	50.04	1.0063	0.9783	2.8	1.3762	1.3670	0.329	1.140	0.989	–13	+1	*4*
Ethylene glycol monoethyl ether	0.9253	1.4057	0.9430	51.95	50.09	0.9903	0.9598	3.1	1.3812	1.3705	0.351	1.103	0.948	–11	+7	*4*
Ethylene glycol monobutyl ether	0.89664	1.4173	0.9690	52.17	49.52	0.9588	0.9447	1.5	1.3812	1.3767	0.319	1.244	1.076	–11	–3	*4*
Diethylene glycol monomethyl ether	1.0167	1.4245	0.9161	49.32	49.81	1.0339	1.0068	2.6	1.3867	1.3779	0.325	1.156	0.994	–14	–1	*3*
Diethylene glycol monoethyl ether	0.9841	1.4254	0.9333	49.98	49.65	1.0209	0.9906	3.0	1.3892	1.3789	0.340	1.126	0.967	–13	+3	*3*
Diethylene glycol monobutyl ether	0.9484	1.4299	0.9557	52.96	51.71	0.9900	0.9713	1.9	1.3906	1.3841	0.348	1.137	0.977	–9	+1	*3*
Diethylene glycol dimethyl ether	0.9384	1.4058	0.9366	46.78	45.28	1.0060	0.9696	3.6	1.3791	1.3668	0.338	1.122	0.965	–15	+3	*33*
Monoethanol amine	1.0127	1.4521	0.9457	48.96	49.35	1.0193	1.0047	1.4	1.3957	1.3911	0.315	1.238	1.066	–11	–3	*32*
Diethanol amine	1.0935	1.4760	0.9292	48.13	50.44	1.0588	1.0435	1.5	1.4060	1.4016	0.288	1.340	1.173	–15	–8	*32*
Triethanol amine	1.1217	1.4835	0.9226	46.29	49.24	1.0758	1.0548	1.9	1.4089	1.4024	0.310	1.231	1.053	–5	–3	*32*
Diethylene triamine	0.9492	1.4815	1.0069	49.77	48.55	1.0250	0.9732	5.1	1.4254	1.4066	0.363	1.151	0.979	–28	+4	*25*
Triethylene tetramine	0.9769	1.4954	1.0069	50.30	49.79	1.0392	0.9869	5.0	1.4328	1.4145	0.350	1.200	1.018	–37	–3	*25*
Tetraethylene pentamine	0.9906	1.5029	1.0076	49.45	49.28	1.0474	0.9939	5.1	1.4357	1.4168	0.353	1.187	1.006	–35	–1	*25*

[a] % volume decrease = $\left(\frac{1}{d_L} - \frac{1}{d}\right)\frac{1}{d_L} \times 100$. [b] Δn calculated from known Δd and values of d_L and n_L. [c] Data of Buchkremer (*1*) for acetic acid and water at 20° C. give the same slopes. For the last 5 columns of this table, his data give the following numbers: 0.391; 0.869; 0.761; +17; +31.

at the correct refractive index within 1 to 4 units in the 4th decimal for the three compounds in this series is significant. The total refractive index increment in this case is approximately 188 units in the 4th decimal. The accuracy with which Δn is calculated for this series is therefore about 1 to 2% of Δn.

The Newton, (or Sellmeier-Drude) function also represents the relation between n and d for groups of hydrocarbon isomers at constant temperature (*11, 15, 16, 17*) and pressure. In this case, as in the case of volume change on mixing, there is a change in free volume at constant temperature and pressure, and a constant number and frequency of dispersion electrons. The Sellmeier-Drude equation (*4*) should always apply at constant temperature and pressure, if the number of dispersion electrons, and their frequency, do not change.

LINEARITY OF PROPERTIES FOR BINARY MIXTURES

Another aspect of data for binary mixtures which is of interest is the degree of linearity of various properties. Aqueous blends of acetone, methyl alcohol, ethylene glycol monomethyl ether, monoethanol amine, and tetraethylenepentamine were selected to illustrate these effects. Table IV gives specific refractions for these pure compounds and for water. Table V gives the ideal volume % of the blends; Δ_1, the difference in property between water and the organic component; Δ_2, the difference between the observed property and the property calculated for the ideal blend (no volume change on mixing) and finally the ratio of Δ_2/Δ_1 expressed as %. This table shows clearly that the effect of volume change on mixing can be a large proportion of the total difference in properties between water and the organic compound. In the case of tetraethylenepentamine, the density difference Δ_1 is not large and Δ_2/Δ_1 is 823%. In the case of methyl alcohol, the refractive index difference Δ_1 is small and Δ_2/Δ_1 is 193%. This is emphasized because, if analysis is being considered, a physical property or physical property function, should be picked which provides a large difference in property between water and the organic compound in question. The refractivity intercept provides a substantial value for Δ_1 for the blends studied, but the value of Δ_2/Δ_1 for the blends shown is still in the range 2 to

Table IV. Specific Refraction, 25° C., for Pure Compounds

	$(n^2-1)/\mathrm{d}$	$(n-1)/\mathrm{d}$	$\left(\frac{n^2-1}{n+0.4}\right)\frac{1}{\mathrm{d}}$	$\left(\frac{n^2-1}{n^2+2}\right)\frac{1}{\mathrm{d}}$
Acetone	1.0676	0.4532	0.6080	0.2781
Methyl alcohol	0.9656	0.4150	0.5593	0.2659
Ethylene glycol monomethyl ether	1.0002	0.4167	0.5556	0.2525
Monoethanol amine	1.0946	0.4464	0.5910	0.2664
Tetraethylene pentamine	1.2706	0.5076	0.6677	0.2983
Water	0.7778	0.3335	0.4490	0.2060

Table V. Deviation from Linearity of Properties of Binary Solutions

		Density			Refractive Index			Refractivity Intercept[a]		
Organic Component	Ideal Vol. %	$\Delta_1 \times 10^4$	$\Delta_2 \times 10^4$	Δ_2/Δ_1, %	$\Delta_1 \times 10^4$	$\Delta_2 \times 10^4$	Δ_2/Δ_1, %	$\Delta_1 \times 10^4$	$\Delta_2 \times 10^4$	Δ_2/Δ_1, %
Acetone	56.05	−2118	+383	18	+234	+147	63	+1293	−45	3.5
Methyl alcohol	55.55	−2105	+328	15.6	−60	+116	193	992	−48	4.8
Ethylene glycol monomethyl ether	50.98	−368	+280	76	+677	+92	13.7	861	−48	5.6
Monoethanol amine	48.96	+156	+145	93	+1196	+47	3.9	1118	−27	2.3
Tetraethylenepentamine	49.45	−65	+535	823	+1704	+189	11.1	1736	−79	4.6

	Newton[b]			Gladstone and Dale[c]			Eykman[d]			Lorentz-Lorenz[e]		
Organic Component	$\Delta_1 \times 10^4$	$\Delta_2 \times 10^4$	Δ_2/Δ_1, %	$\Delta_1 \times 10^4$	$\Delta_2 \times 10^4$	Δ_2/Δ_1, %	Δ_1	Δ_2	Δ_2/Δ_1, %	Δ_1	Δ_2	Δ_2/Δ_1, %
Acetone	2899	+48	1.7	+1197	−4	0.3	1591	−17	1.1	721	−13	1.8
Methyl alcohol	1878	+26	1.4	816	−7	0.8	1102	−18	1.6	508	−12	2.4
Ethylene glycol monomethyl ether	2224	+14	0.6	833	−13	1.6	1066	−24	2.2	465	−14	3.0
Monoethanol amine	3169	−8	0.2	129	−11	1.0	1421	−18	1.2	604	−10	1.7
Tetraethylenepentamine	4928	−3	0.6	1742	−34	1.9	2188	−59	2.7	923	−34	3.7

[a] $n - \mathrm{d}/2$. [b] $\frac{n^2-1}{\mathrm{d}}$. [c] $\frac{n-1}{\mathrm{d}}$. [d] $\left(\frac{n^2-1}{n+0.4}\right)\frac{1}{\mathrm{d}}$. [e] $\left(\frac{n^2-1}{n^2+2}\right)\frac{1}{\mathrm{d}}$.

Δ_1 = property of organic compound − property of Water

Δ_2 = property observed for blend − property calculated by linear interpolation on ideal vol. % basis

Table VI. % Composition by Interpolation

	Composition		Composition by Linear Interpolation				
Organic Component	Ideal vol. %	Wt. %	$n - \mathrm{d}/2$	$(n^2-1)/\mathrm{d}$	$(n-1)/\mathrm{d}$	$\left(\frac{n^2-1}{n+0.4}\right)\frac{1}{\mathrm{d}}$	$\left(\frac{n^2-1}{n^2+2}\right)\frac{1}{\mathrm{d}}$
Acetone	56.05	50.11	52.8	52.0	50.0	49.3	48.6
Methyl alcohol	55.55	49.64	50.8	51.2	48.8	47.6	47.3
Ethylene glycol monomethyl ether	50.98	50.04	45.4	49.7	48.4	47.9	47.4
Monoethanol amine	48.96	49.35	47.3	48.7	49.2	48.4	49.7
Tetramethylenepentamine	49.45	49.28	44.9	47.8	47.9	47.1	47.1

6%. This is much better than the density or refractive index for linearity, but as shown in Table V the Newton specific refraction, $(n^2 - 1)/d$, and the Gladstone and Dale specific refraction, $(n - 1)/d$, show values of Δ_2/Δ_1 of 0.1 to 2.0%. For the Eykman specific refraction, and the Lorentz-Lorenz specific refraction, Δ_2/Δ_1, is somewhat larger than for the Newton and Gladstone and Dale specific refraction.

Table VI shows % composition calculated by interpolation, which is often done in the analysis of binary mixtures. For comparison the known ideal volume % and weight % are also shown. Consider first the % composition calculated from refractivity intercept, which should agree with ideal volume %. For the last three blends, where the difference between ideal volume % and weight % is small, the calculated % is lower than either the volume or weight %. If the % deviation shown for refractivity intercept in Table V is added to the % composition shown in the $(n - d)/2$ column in Table VI, agreement with the ideal volume % is nearly perfect for all five blends. This shows the way in which deviation from linearity influences the calculated % composition for refractivity intercept.

In the case of the Lorentz-Lorenz specific refraction

$$\left(\frac{n^2-1}{n^2+2}\right)\frac{1}{d}$$

one would expect the function to be linear with weight % rather than volume %. Adding the deviation shown in the last column of Table V to the last column in Table VI gives a good check for the first three blends. For the last two blends, the deviation is 1.6 to 1.8%.

The per cent composition calculated from all the specific refraction equations agree reasonably well, but the Newton and Gladstone-Dale specific refractions give per cent compositions which are more nearly correct than per cent composition calculated from the other specific refractions.

CONCLUSIONS

This analysis of data for certain binary aqueous mixtures shows the desirability of calculating ideal volume per cent and the corresponding values of density, refractive index, etc., for the hypothetical ideal mixtures without volume change on mixing. The change from these ideal properties to the observed properties provides an approach to the study of nonideality which is quite revealing and suggests the desirability of obtaining data for refractive index for several wavelengths for binary mixture blends, so that the apparent number and frequency of the dispersion electrons can be calculated with the Sellmeier-Drude dispersion equation.

For many purposes, it is desirable to consider binary mixtures from the point of view of mole per cent composition (*9, 10, 24, 26, 27, 33*). However, in dealing with mole per cent composition of aqueous solutions the extreme difference in size of the water molecules and the dissolved organic molecules leads to an unfortunate compression of about half of the volume per cent composition range into the first 10% of the mole per cent composition scale (*33*). In dealing with density, refractive index, and similar properties, this is a distinct disadvantage in the use of mole % composition.

That the Newton (or Sellmeier-Drude) function, $(n^2 - 1)/d$ = constant, correlates well the relation between refractive index and density for many binary aqueous blends is significant in connection with refraction theory and free volume theory. The hypothesis is presented that when hydrogen bonding is low the Sellmeier-Drude function represents the data well.

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