

A Note on the Specific Refractive Index Increments for Poly (2-methyl-5-vinyl pyridine) Solutions

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The information of the specific refractive index increment of a solution, dn/dc , is mainly required to the determination of molecular weights of polymer by light scattering, which is defined as $(n-n_1)/c$, where n , n_1 , and c are the refractive indices for the solution, the solvent and the concentration of solute (in grams per milliliter), respectively. A precise knowledge of the specific increment is, moreover, a prerequisite not to incur an uncertainty in molecular weights, because it enters as a square term in the constant K of the basic equation of light scattering.

However, the value is not a characteristic constant of a given polymer, but depends on the temperature, the pressure, the wavelength of light and the nature of solvent, and their measurements are delicate and mistakable. Though R. Chiang¹) also emphasized an importance of the precision of dn/dc values in his book, few discussions have been made about these problems till now.

Conventionally it is known that the empirical relation of Gladstone-Dale is held among the natures of solvent and solute, and their increments, which may be convenient to calculate the value of dn/dc in other solvents and at other temperatures from data already known, provided the highest accuracy is not required.

In this paper, the application of the relation to poly (2-methyl-5-vinyl pyridine)-solvent systems and its validity were discussed briefly, considering the condition under which this rule is established.

Equations of Gladstone-Dale and Lorenz-Lorentz

The empirical rule of Gladstone and Dale (G-D eq.) is as follows

$$dn/dc = r_2 - (d_1/d_2)r_1 \quad (1)$$

$$r_2 = (n_2 - 1)/d_2, \quad r_1 = (n_1 - 1)/d_1$$

where d is the density, and r , the specific refractivity denoted generally $(n_i - 1)/d_i$ which is a constant independent of temperature and the subscripts 1 and 2 refer to the solvent and the solute (polymer), respectively.

Eq. (1) may be simplified as

$$dn/dc = (n_2 - n_1)/d_2 \quad (2)$$

Hence plots of dn/dc against n_1 should be a straight line with a negative slope, and then d_2 and n_2 may be obtained from the inverse slope and the intercept at $dn/dc=0$, respectively.

Recently, Huglin²⁾ reviewed that the G-D rule was established on two assumptions of additivities of r_i and volumes for a mixture.

Namely the specific refractivity r and the density d of a binary solution may be written

$$r = w_1 r_1 + w_2 r_2 \quad (3)$$

$$1/d = w_1/d_1 + w_2/d_2 \quad (4)$$

Here w is the weight fraction. Denoting $w_2 d$ by the concentration c , it is easily realized that eq. (2) is derived from these equations.

An attempt was also made to deduce a similar expression with a sounder theoretical basis than the G-D eq. from the specific refraction R_i proposed by Lorenz and Lorentz, which is written as

$$R_i = (n_i^2 - 1)/d_i(n_i^2 + 2)$$

Now, if two assumptions of additivity are made similarly as mentioned above

$$R = w_1 R_1 + w_2 R_2 \quad (5)$$

$$1/d = w_1/d_1 + w_2/d_2$$

As a result, for a binary system

$$\begin{aligned} (n^2 - 1)/(n^2 + 2) - (n_1^2 - 1)/(n_1^2 + 2) = \\ (c/d_2) [(n_2^2 - 1)/(n_2^2 + 2) - (n_1^2 - 1)/(n_1^2 + 2)] \end{aligned} \quad (6)$$

The function $(n_i^2 - 1)/(n_i^2 + 2)$ varies monotonously with a slightly upward curvature against n_i and also the difference between n and n_1 is extremely small because the solution used to measure is fairly dilute.

Hence we can write

$$(n^2 - 1)/(n^2 + 2) - (n_1^2 - 1)/(n_1^2 + 2) = \Delta n \cdot s \quad (7)$$

$$s = 6n_1/(n_1^2 + 2)^2$$

where Δn is equal to $(n - n_1)$ and s , the slope of the curve at n_1 .

Finally, from eq. (6) and eq. (7) we get

$$\begin{aligned} (dn/dc) = \Delta n/c = \\ [(n_2^2 - 1)/(n_2^2 + 2) - (n_1^2 - 1)/(n_1^2 + 2)](n_1^2 + 2)^2/6n_1d_2 \end{aligned} \quad (8)$$

This equation (L-L eq.), though complicated yet, was deduced instead of the G-D eq., with a theoretical basis. From this, dn/dc and n_2 are estimated from an appropriate calculation.

Experimental

Preparation of poly (2-methyl-5-vinyl pyridine) (PMVP) 2-methyl-5-vinyl pyridine monomer was distilled immediately before use in a usual manner (b. p. 62°~63° C/10

mmHg). The bulk polymerization was carried out at 70°C for a week in a nitrogen atmosphere with 0.31% benzoyl peroxide as an initiator. The conversion rate was about 95.6%. The polymer produced was fractionally precipitated³⁾ in seven fractions with methanol as a solvent and water as a precipitant. As a result, a middle fraction was used for measurements mentioned below, whose molecular weight was about 79×10^4 from viscosity measurements in methanol at 25°C.

Solvents The solvents used in this work were fractionally distilled by usual methods, but a part, commercial reagents of special grade were used.

Specific refractive index increments The refractive index increments were measured in ten different solvents by a Brice type differential refractometer (Shimadzu Seisakusho, DR-3 type) at 25°C with the blue (436 $m\mu$) and green (546 $m\mu$) lights, which was calibrated by means of the aqueous potassium chloride solution.

At the same time the refractive indices of solvents were determined by an Abbe refractometer (Atago Kogakukikai) at 25°C, and the indices at 436 $m\mu$ and 546 $m\mu$ were evaluated with the aid of values of the dispersive power measured.

Results and Discussion

It may be supposed that the PMVP sample induces appreciable intermolecular interactions in various solvents for pyridine nitrogens of its side group, and partially ionizes in the very extreme. The preliminary examination was conducted in order to estimate to what extent these assumptions were acceptable in the case of PMVP-solvent systems, which was to measure the corresponding changes of the refractive indices against the weight fractions of a binary mixture between pyridine and the other solvent. Pyridine was, for brevity, chosen from the supposition of an approximately similar behavior to the monomer unit of PMVP.

Table I. Variations of the refractive indices against the weight fractions of binary pyridine solutions at 25°C

solvent	w_2	n_{25D}^{25}	d_0	d_{L-L}	$\Delta_{L-L}(\%)$	d_{G-D}	$\Delta_{G-L}(\%)$
			from eq. (4)	from eq. (5)		from eq. (3)	
chloroform	0.0	1.4428	1.4796				
	0.104	1.4526	1.4046	1.4060	0.10	1.4053	0.05
	0.221	1.4645	1.3290	1.3363	0.55	1.3364	0.55
	0.351	1.4734	1.2539	1.2592	0.42	1.2588	0.39
	0.498	1.4830	1.1785	1.1837	0.44	1.1830	0.38
	0.665	1.4921	1.1033	1.1068	0.32	1.1062	0.26
	0.856	1.5009	1.0282	1.0298	0.15	1.0292	0.10
	1.0	1.5069	0.9780				
dioxane	0.0	1.4199	1.0269				
	0.144	1.4329	1.0195	1.0208	0.13	1.0196	0.01
	0.290	1.4461	1.0122	1.0145	0.23	1.0126	0.04
	0.436	1.4589	1.0050	1.0070	0.20	1.0053	0.03
	0.588	1.4721	0.9976	0.9993	0.17	0.9977	0.01
	0.741	1.4855	0.9902	0.9921	0.19	0.9911	0.09
	0.896	1.4982	0.9829	0.9840	0.12	0.9829	0.00

Table I. (continued)

solvent	w_2	n_D^{25}	d_0	d_{L-L}	$\Delta_{L-L}(\%)$	d_{G-D}	$\Delta_{G-D}(\%)$
			from eq. (4)	from eq. (5)		from eq. (3)	
methylethyl ketone	0.0	1.3762	0.7995				
	0.178	1.3962	0.8262	0.8287	0.30	0.8272	0.12
	0.344	1.4167	0.8529	0.8584	0.64	0.8559	0.35
	0.498	1.4366	0.8793	0.8857	0.72	0.8833	0.46
	0.647	1.4561	0.9064	0.9122	0.64	0.9097	0.36
	0.786	1.4752	0.9333	0.9375	0.45	0.9355	0.23
	0.917	1.4933	0.9601	0.9607	0.06	0.9592	-0.09
water	0.0	1.3327	0.9971				
	0.148	1.3601	0.9942	1.0005	0.63	0.9978	0.36
	0.296	1.3868	0.9913	1.0009	0.97	0.9964	0.52
	0.445	1.4141	0.9885	1.0008	1.24	0.9962	0.78
	0.595	1.4417	0.9857	1.0000	1.45	0.9962	1.07
	0.746	1.4685	0.9828	0.9965	1.40	0.9941	1.15
	0.898	1.4928	0.9799	0.9878	0.81	0.9869	0.71
methanol	0.0	1.3262	0.7868				
	0.180	1.3563	0.8153	0.8253	1.22	0.8225	0.88
	0.348	1.3848	0.8441	0.8583	1.68	0.8540	1.18
	0.504	1.4122	0.8726	0.8877	1.73	0.8831	1.20
	0.651	1.4392	0.9014	0.9155	1.56	0.9111	1.07
	0.789	1.4660	0.9302	0.9419	1.26	0.9388	0.92
	0.918	1.4899	0.9588	0.9631	0.45	0.9612	0.25

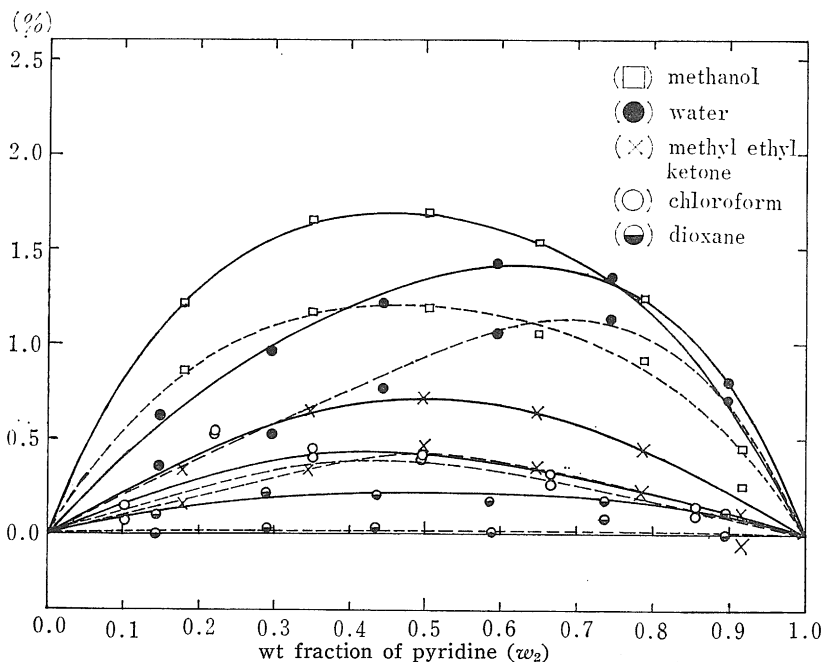


Fig. 1 Plots of the deviation (Δ) vs. the weight fraction (w_2) of pyridine at 25°C, full curve—plots of Δ_{L-L} vs. w_2 , broken curve—plots of Δ_{G-D} vs. w_2 .

These results measured for five solvents are listed in Table I, where the symbols d_0 , d_{L-L} and d_{G-D} are, respectively, the densities calculated from eq. (4), eq. (5) and eq. (3), and Δ , the degree of deviation from d_0 . These are also illustrated in Fig. 1.

As shown in the figure, the deviation from assumption is generally smaller in the G-D eq. rather than that of the L-L eq. In dioxane the smallest deviation was denoted in either equations as might be expected. Especially the pyridine-dioxane mixture is supposed to be applicable to the G-D eq. satisfactorily, and to the L-L eq. pretty well. The difference between n and n_1 are actually only about 0.3% at most and hence the values of the specific increments in the other mixtures may be affected by the nature of solvents to some extent, though solutions are diluted. For instance, the specific increment of pyridine in methanol was overestimated by 15.7% from the results of Fig. 1, compared with the value expected from the right hand in eq. (2).

Table II. The results of the indices of refraction and the refractive index increments in various solvents at 25°C and at the wavelength of 436 $m\mu$ and 546 $m\mu$.

solvent	n^{25}_{436}	n^{25}_{546}	$(dn/dc)_{436}$	$(dn/dc)_{546}$
methanol	1.331	1.327	0.267	
ethanol	1.365	1.361	0.238	0.224
isopropanol	1.382	1.376	0.217	0.201
methylethylketone	1.384	1.377	0.210	
nitromethane	1.388	1.383	0.172	
tetrahydrofuran	1.411	1.406	0.191	
dioxane	1.426	1.421	0.174	0.156
chloroform	1.451	1.444	0.145	
benzene	1.514	1.502	0.097	0.094
chlorobenzene	1.543	1.526	0.061	
methanol#	1.331	1.327	0.288	0.279
water#	1.338	1.334	0.265	0.259

#) The solute is the PMVP partially quarternized by HCl.

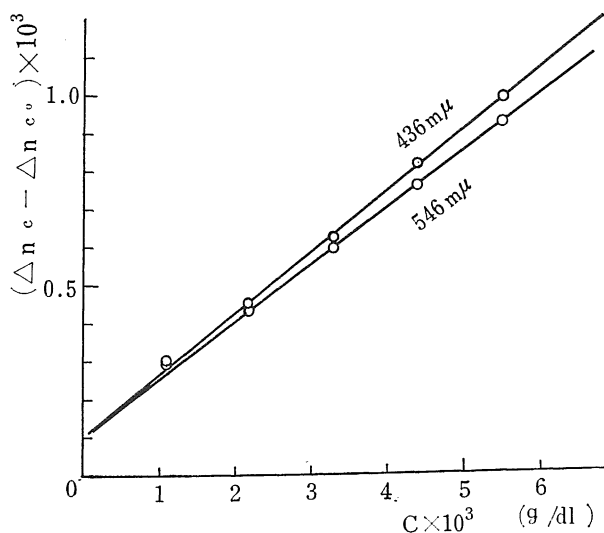


Fig. 2 Plots of the difference of the refractive indices between the solution and the solvent against the concentration in dioxane at 25°C.

In Table II are shown the results of dn/dc of PMVP in various solvents at 25°C together with their refractive indices measured and in Fig. 2 the plots of the result in dioxane as a typical example.

And then the data of the last two rows in the table are that of PMVP appropriately quarternized by hydrogen chloride. These increments dn/dc were plotted against n_1 in

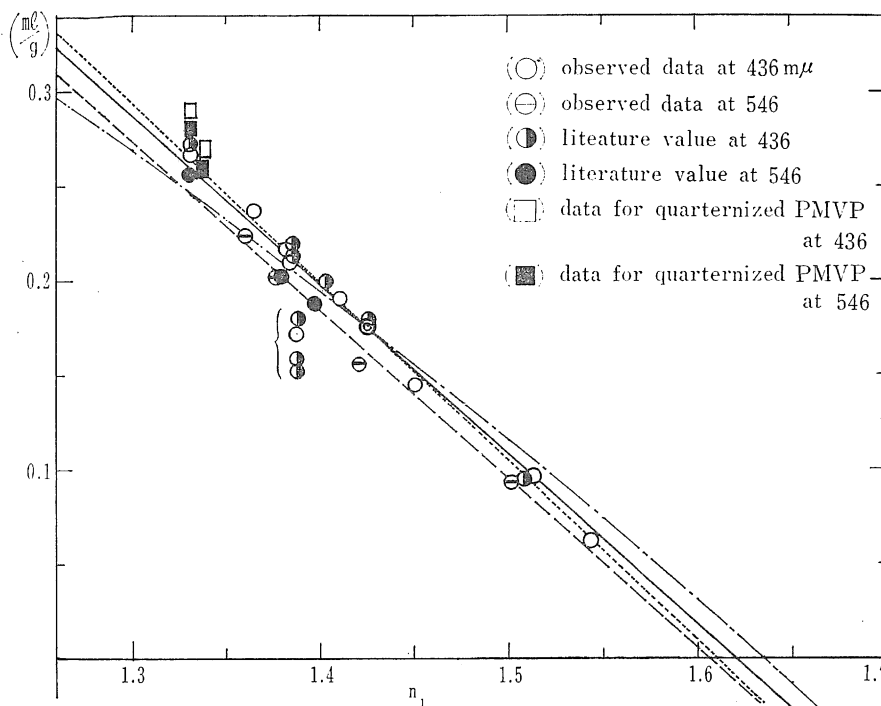


Fig. 3 Plots of dn/dc vs. n_1 at 25°C.

Dotted line is for G-D eq. obtained apparently from the experimental points at 436 $m\mu$. Full line for G-D eq. based on the data observed in dioxane (⊙) at 436 $m\mu$. Chain line for L-L eq. in the similar case. Broken line for that at 546 $m\mu$ corresponding to full line.

Table III. A list of the literature values of poly (2-methyl-5-vinyl pyridine) in various solvents, which have been published by this.

solvent	n_{25}^{436}	n_{25}^{546}	$(dn/dc)_{436}$	$(dn/dc)_{546}$	ref.
methanol			0.273	0.257	(3)
methylethylketone			0.219		"
	1.385	1.378	0.212	0.202	(6)
nitromethane			0.180 ^a		(5)
			0.159 ^b		"
			0.152 ^c		"
buthyl acetate	1.404	1.397	0.200	0.188	(6)
dioxane			0.180		(3)
toluene	1.509 [#]		0.0951		(3)

a) 0.60 g./ml b) 0.40 g./ml c) 0.20 g./ml #) observed value in this laboratory

Fig. 3, where for comparison the literature values published by this were also plotted, which were summarized in Table III.

Now, apparently the G-D eq. seems to be established within experimental errors, concerning about the data at 436 $m\mu$ in the figure. The relation estimated by the least square method was as follows (designated by the dotted line in the figure).

$$dn/dc = (1.069 - n_1)/1.044 \quad (9)$$

From this, the values of n_2 and d_2 were apparently obtained 1.069 and 1.044, respectively, but these values may be supposed to be uncertain, judging from the preceding examinations.

On the other hand, the density of this polymer in bulk at 25°C was measured as 1.113 by floating the polymer film in a mixed solvent of ligroin and carbon tetrachloride carefully. The value was comparative with that of Gechele et. al.⁴, 1.110, though variable a little by the preparation method adopted.

Utilizing this value, the refractive index of polymer, n_2 , at 436 $m\mu$ was calculated as 1.620 from the G-D eq. based on the data in dioxane (shown with a double circle in the figure) which may be supposed satisfactory to be applicable to the equation as mentioned above. Similarly the refractive index computed from the L-L eq. was 1.635. In Fig. 3, the solid and chain lines represent the former and the latter relations, respectively. (Plots of a few data at 546 $m\mu$ were also shown with a broken line and n_2 at the wavelength was presumed about 1.605.)

Consequently, in an ideal the following equation was seemed approximately to be suitable in the PMVP-solvent systems, namely

$$(dn/dc) = (1.620 - n_1)/1.113 \quad (10)$$

And hence values of dn/dc may increasingly deviate from the above equation according to the extent of polymer-solvent interactions

By the way, the plots marked with a parenthesis are that in nitromethane in the figure, and deviate downward greatly beyond expectation. It was hard to elucidate whether this was caused by an unstability of the solvent or a somewhat strong, special interaction between this polymer and nitromethane, but this might be concerned with the anomalous light scattering in the similar systems reported by Cashin⁷ and Seely⁵.

The squares denoted in Fig. 3 also illustrate the plots of partially quarternized PMVP in methanol and in water, for reference. From this behavior, the values of the increments may be supposed to be fairly affected by the nature of solvents, if this polymer was ionized by the cause of the other impurities and/or the strong molecular interactions in solution.

In conclusion, the application of the Gladstone-Dale eq. to the solutions of PMVP was apparently made pretty well, but the attention must be paid for the rigorous analysis, for in these systems the fairly strong interactions may exist in some cases (such as in the alcohols). And also the equation derived from Lorentz-Lorenz eq. was not suitable in the case in spite of their sounder theoretical basis.

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