ON THE REFRACTIVE INDICES OF ETHYLENE CHLORIDE, 1, 1, 2, 2,-TETRACHLORETHANE AND OF THEIR MIXTURE AND THE MOLAR REFRACTIONS OF THESE SUBSTANCES.

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Received June 10th, 1933. Published October 28th, 1933.

In connection with our study on the chemical reactions of some of chlorine derivatives of lower hydrocarbon, we are confronted with the necessity of knowing the refractive indices of these solvents and of their binary mixture. Refractive indices have been measured with an ordinary method using Pulfrich Refractometer (Carl Zeiss). The temperature of the solvent vessel and of the prism have been kept constant by passing the water which is kept constant temperature within $\pm 0.1°$ during measurements.

The materials have been purified by fractional distillation several times and only the middle portions were used.

Ethylene chloride: Takeda's product	B.P. 83.0°C.
1, 1, 2, 2,-Tetrachlorethane: Kahlbaum	B.P. 145.0°C.

For both ethylene chloride and tetrachlorethane, the refractive indices have been observed at various temperatures using H_α line ($\lambda = 656.8$ mμ) and the results were plotted as a function of temperature as shown in Figs. 1 and 2. For the binary mixture ($N_2 = 0.782$) also as shown in Fig. 3 the refractive indices were plotted against the reciprocals of the absolute temperatures. Variation of the refractive index of the binary mixture of ethylene chloride and 1, 1, 2, 2,-tetrachlorethane with the molal fractions has also been studied. The results are given in Fig. 4. All of the above results are also tabulated in the tables 1 to 6 respectively.

Figs. 1, 2 and 3 immediately would show that in each case the refractive index is linearly dependent on the reciprocals of the absolute temperatures within the range of temperature we have studied. The shape of the curve for the binary mixture as plotted against the molal fractions of tetrachlorethane is somewhat convex upward.

For the sake of practical convenience the refractive indices of both ethylene chloride and of tetrachlorethane at round temperature, and in the case of the binary mixture at round molal fractions are given in the table 5 for the range of 10°–30°C. and in the table 6 respectively.

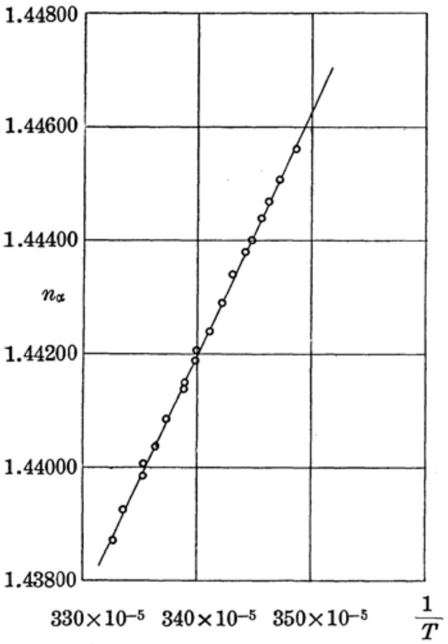

Fig. 1. Refractive indices of ethylene chloride as a function of temperature.

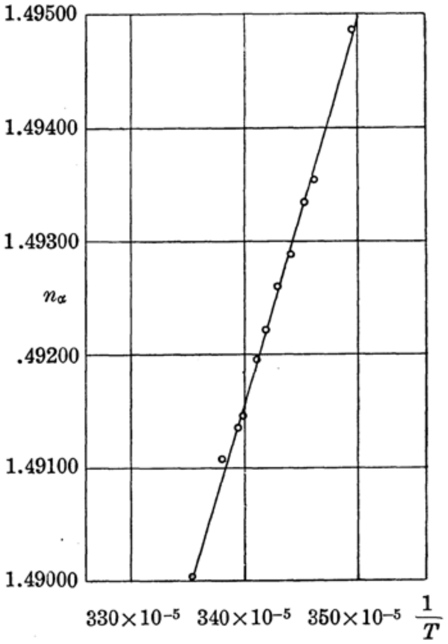

Fig. 2. Refractive indices of 1, 1, 2, 2,-tetrachlorethane as a function of temperature.

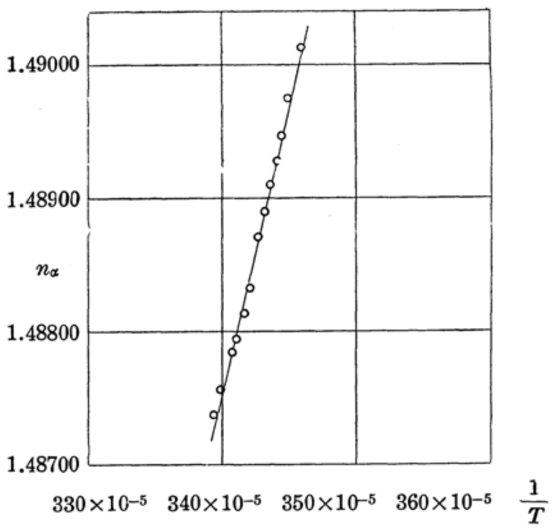

Fig. 3. Refractive indices for ethylene chloride—1, 1, 2, 2,-tetrachlorethane mixture, as a function of temperature of $N_2 = (0.782)$ (1, 1, 2, 2,-tetrachlorethane).

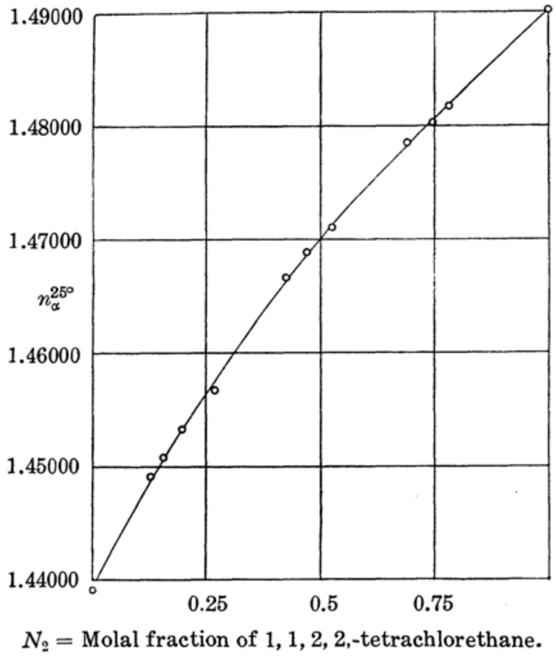

Fig. 4. Variation of index of refraction with respect to the mol. fraction of 1, 1, 2, 2,-tetrachlorethane in the mixture of ethylene chloride and tetrachlorethane at 25°C.

Table 1.
(Ethylene chloride).

t^0 C.	T	$\frac{1}{T}10^{-5}$	n_α	n_α
14.0	287.1	348.6	1.44561	* = different sample
15.0	288.1	347.1	1.44510	
15.7	288.8	346.2	1.44470	
16.2	289.3	345.6	1.44440	
17.0	290.1	344.7	1.44400	
17.5	290.6	344.1	1.44380	
18.5	291.6	342.9	1.44341	
19.1	292.2	342.2	1.44290	
20.0	293.1	341.1	1.44240	1.44239*
21.1	294.2	339.9	1.44189	1.44208*
22.0	295.1	338.9	1.44138	1.44148*
23.6	296.7	337.3	1.44088*	
24.1	297.2	336.4	1.44038	
25.0	298.1	335.4	1.43987	
26.8	299.9	333.4	1.43927*	
27.0	300.1	333.2	1.43927	
27.4	300.5	332.7	1.43866	

Table 2.

(1, 1, 2, 2,-Tetrachlorethane).

t^0 C.	T	$\frac{1}{T}\times10^{-5}$	n_α
13.0	286.1	349.5	1.49486
15.7	288.8	346.2	1.49354
16.5	289.6	345.3	1.49345
17.5	290.6	344.1	1.49298
18.5	291.6	342.9	1.49260
19.3	292.4	341.9	1.49222
20.0	293.1	341.1	1.49196
21·1	294.2	339.9	1.49146
21.4	294.5	339.5	1.49136
22.0	295.1	338.9	1.49108
25.0	298.1	335.4	1.49004

$C_2H_4Cl_2$		Authors	B.P.
t^0	n_α		
20.0	1.44189	(Brühl, *Ann.* **203** (1880) 1)	84.5–85° at 750.9 mm.
21.2	1.44218	(Kanonnikoff, *Z. prakt. Chem.*, **32** (1885), 497)	83.5–84°
21.4	1.44213		
21.8	1.44206		
22.1	1.44184		

$C_2H_2Cl_4$		Authors	B.P.
t^0	n_α		
18.5	1.49209	(Veley, *Phil. Mag.*, **11** (1906) 73)	
21.8	1.49155	(Kanonnikoff, *Z. prakt. Chem.*, **32** (1885), 497)	146°
22.0	1.49148		
22.2	1.49143		
22.4	1.49127		

Table 3.

Mixture of ethylene chloride and 1, 1, 2, 2,-tetrachlorethane
$N_2 = 0.782$ (tetrachlorethane).

t^0 C.	T	$\frac{1}{T} \times 10^{-5}$	n_α
16.0	289.1	345.9	1.49013
16.8	289.9	344.9	1.48975
17.2	290.3	344.4	1.48947
17.5	290.6	344.1	1.48928
17.9	291.0	343.6	1.48910
18.2	291.3	343.2	1.48890
18.7	291.8	342.7	1.48871
19.2	292.3	342.1	1.48833
19.5	292.6	341.7	1.48814
20.0	293.1	341.1	1.48795
20.3	293.4	340.8	1.48785
21.1	294.2	339.9	1.48757
21.6	294.7	339.3	1.48738

Table 4.

Refractive index of mixture $C_2H_4Cl_2$ and 1, 1, 2, 2,-$C_2H_2Cl_4$ at 25°C.

N_2	n_α	N_2	n_α
0.000	1.43990	0.470	1.46884
0.129	1.44903	0.525	1.47109
0.156	1.45074	0.687	1.47861
0.198	1.45324	0.748	1.48035
0.270	1.45664	0.782	1.48171
0.425	1.46617	1.000	1.49004

Table 5.

Refractive indices of ethylene chloride and 1, 1, 2, 2,-tetrachlorethane at various temperatures as obtained from the graphs.

t^0 C.	$C_2H_4Cl_2$		$C_2H_2Cl_4$	
	n_g	n_{ob}	n_g	n_{ob}
10	1.44765		1.49600	
11	1.44716		1.49563	
12	1.44673		1.49520	
13	1.44611		1.49477	1.49486
14	1.44573	1.44561	1.49447	

Table 5.—(*Concluded*)

t^0 C.	$C_2H_4Cl_2$		$C_2H_2Cl_4$	
	n_g	n_{ob}	n_g	n_{ob}
15	1.44510	1.44510	1.49396	
16	1.44455		1.49356	
17	1.44400	1.44400	1.49315	
18	1.44350		1.49275	
19	1.44300		1.49238	
20	1.44240	1.44240	1.49194	1.49196
21	1.44195		1.49155	
22	1.44144	1.44138	1.49120	1.49108
23	1.44095		1.49080	
24	1.44045		1.49038	
25	1.43990	1.43987	1.49003	1.49004
26	1.43946		1.48965	
27	1.43900	1.43927	1.48928	
28	1.43850		1.48890	
29	1.43800		1.48854	
30	1.43752		1.48817	

n_g = n from the graph
n_{ob} = n as observed

Table 6.

Refractive indices at various mol fractions of the binary mixture of ethylene chloride and 1, 1, 2, 2,-tetrachlorethane at 25°C.

Molal fractions N_2	Refractive indices n_α	Molal fractions N_2	Refractive indices n_α
0.0	1.43987	0.6	1.47460
0.1	1.44680	0.7	1.47880
0.2	1.45340	0.8	1.48260
0.3	1.45930	0.9	1.48650
0.4	1.46490	1.0	1.49004
0.5	1.47000		

Molar Refraction. Molar refraction, in general, can be computed from the formula as derived by Lorenz—Lorentz.(1)

$$P_0 = \frac{(n^2-1)M}{(n^2+2)\rho} \qquad (1)$$

Where: M = molecular weight
ρ = density
n = refractive index
P_0 = molar refraction(2).

If in the expression (1) n is replaced by n_∞ i.e. refractive index for zero frequency, then $P_0 = \frac{n_\infty^2-1}{n_\infty^2+2}\frac{M}{\rho}$ becomes the molar polarization which in general, is not very much different from a in the expression:

$$P = a + \frac{b}{T}^{(3)} \qquad (2)$$

a, the constant is what we called P_0.
The molar refraction P_0 calculated from n_α where H_α line $= 656.3 m\mu$ and the density is taken from the values computed by the expression as given in the International Critical Table namely:

Density for $C_2H_4Cl_2$:

$$d_s = 1.28248 - 1.4217(t-t_s)\times 10^{-3} - 0.933(t-t_s)^2\times 10^{-6} + 2.29(t-t_s)^3\times 10^{-9}$$
$$t_s = 0°C.$$

and for $C_2H_2Cl_4$:

$$d_s = 1.5869 - 1.53(t-t_s)\times 10^{-3} - 0.78(t-t_s)^2\times 10^{-6} + 2.5(t-t_s)^3\times 10^{-9}$$

Thus the P_0 as computed gave very concordant results as are to be shown in the following tables 7 and 8.

Table 7.

The molar refraction for $C_2H_4Cl_2$ $P_0 = \frac{n_\alpha^2-1}{n_\alpha^2+2}\frac{M}{\rho}$

t^0 C.	ρ	n_α	P_0
10	1.26817	1.44765	20.83
15	1.26095	1.44510	20.81
17	1.25805	1.44400	20.83
20	1.25369	1.44240	20.82
25	1.24639	1.43990	20.84
30	1.23904	1.43752	20.80
			Ave. 20.82

(1) L. A. Lorenz, *Wied. Ann.*, **11** (1880) 70; L. A. Lorentz, *Wied. Ann.*, **9** (1880), 641.
(2) Debye's, "Polar Molecules" 1929.
(3) Debye's, "Polar Molecules" p. 57.

Table 8.

The molar refraction for $C_2H_2Cl_4$ $P_0 = \frac{n_\alpha^2-1}{n_\alpha^2+2}\frac{M}{\rho}$

t^0 C.	ρ	n_α	P_0
10	1.57152	1.49600	31.15
15	1.56380	1.49396	31.21
17	1.56070	1.49315	31.21
18.5	1.55830	1.49260	31.21
20	1.55600	1.49194	31.21
25	1.54820	1.49004	31.32
30	1.54040	1.48817	31.31
			Ave. 31.23

For ethylene chloride, H. Jahn and G. Möller[4] have given the value for $P_0 = \frac{n_\alpha^2-1}{n_\alpha^2+2}\frac{M}{\rho} = 20.81$, while Weegmann[5] reported $P_0 = 20.44$ calculated from $n_\infty = 1.431367$. For tetrachlorethane, there is no reference found in connection with the molar refraction as far as the present author knows.

Calculation of Electric Moment for $C_2H_4Cl_2$. Smyth, in 1924 presented a method for calculation of electric moment by extraporating for n_∞[6] but since we know the value $P_0 = 20.44$ of Weegmann for $\lambda = \infty$, combining with those values of $\frac{M}{\rho}\frac{\epsilon^2-1}{\epsilon^2+2}$ as given by various authors as well as the value computed by the present author, the value μ can be calculated.

60.29 (H. Jahn and G. Möller, *Z. physik. Chem.*, **13** (1894) 385).
60.06 (19.8°C.) (Walden, *Z. physik. Chem.*, **70** (1910) 569).
60.42 (20.0°C., $\lambda = \infty$) The present author; using the value of dielectric constant $\varepsilon = 10.8$.
(Joachin, *Ann. Phys.* **60** (1919), 570).

Using $P_0 = 20.44$ (Weegmann) and $\frac{M}{\rho}\frac{\epsilon^2-1}{\epsilon^2-2} = 60.42$ μ is found by:

(4) *Z. physik. Chem.*, **13** (1894), 385.
(5) *Z. physik. Chem.*, **2** (1888), 218.
(6) Smyth, *J. Amer. Chem. Soc.*, **46** (1924), 2151.

$$\mu = 0.0127\sqrt{(P-P_0)T} \times 10^{-18} \text{ (2)} \quad (3)$$

to be 1.375×10^{-18}.

The dielectric constant for tetrachlorethane, hitherto is not found in the literatures so that we were unable to calculate the value of μ, however, the molar refraction has been given in the table already mentioned.

Table 9.

For ethylene chloride.

P_0	Authors	P	Authors
20.44 ($\lambda = \infty$)	Weegmann(7)	60.06	Walden(8) ($t = 19.8°$)
20.81 ($\lambda = H_\alpha$)	Jahn and Möller(9)	60.29 ($t = 20°$)	Jahn and Möller
20.82 ($\lambda = H_\alpha$)	The present author	60.42 ($t = 20°$)	The author's calculation from $\varepsilon = 10.8$, ($\lambda = \infty$) of Joachin(10)

For the sake of comparison μ's of various authors for ethylene chloride in various states are tabulated as follows in the table 10:

Table 10.

Electric moment of ethylene chloride $\mu \times 10^{-18}$				
In benzene	In hexane	In heptane	Liquid	As vapour
1.83(11)	1.26–1.42(11)	1.16–1.42(14)	1.55(15)	1.56(16)
1.86(12)				1.01(17)
1.75(13)			1.375(19)	1.12–1.54(18)

(7) Weegmann, *Z. physik. Chem.*, **2** (1888), 218.
(8) Walden, *Z. physik. Chem.*, **70** (1910), 569.
(9) Jahn and Möller, *Z. physik. Chem.*, **13** (1894), 385.
(10) Joachin, *Ann. Phys.*, **60** (1919), 570.
(11) Meyer, *Z. physik. Chem.*, B **8** (1930), 27.
(12) Gross, *Phys. Zeit.*, **30** (1929), 504.
(13) Williams, *Zeit. f. physik. Chem.*, **138** (1928), 75.
(14) Smyth, *J. Am. Chem. Soc.*, **53** (1931), 4242.
(15) Walden, *Z. physik. Chem.*, **70** (1910), 569.
(16) Ghosh Mahanti and Sen Gupta, *Z. physik.*, **54** (1929), 711.
(17) Sänger, *Physik. Z.*, **32** (1931), 21.
(18) Zahn, *Phys. Rev.*, **38** (1931), 52.
(19) The author's calculation.

In conclusion, the author wishes to express his thanks to Prof. S. Mitsukuri for his kind advices.

Summary.

(1) Refractive indices of ethylene chloride, 1, 1, 2, 2,-tetrachlorethane and their binary mixture have been measured.

(2) Variation of the refractive index with respect to temperature and to the molar fractions at 25°C. have been studied.

(3) Linear dependence of the refractive index on the reciprocals of absolute temperature in each case was observed.

(4) Refractive index at round temperature for ethylene chloride and 1, 1, 2, 2,-tetrachlorethane and refractive index at round molal fraction for the binary mixture at 25°C. have been tabulated.

(5) The molar refraction for both ethylene chloride and 1, 1, 2, 2,-tetrachlorethane have been calculated as 20.82 and 31.23 respectively.

(6) The electric moment μ has been calculated for liquid ethylene chloride to be 1.375×10^{-18}.

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