ADIABATIC PIEZO-OPTIC COEFFICIENTS OF LIQUIDS

(Ethyl Acetate, Methyl Acetate, Amyl Acetate and Cyclohexanol)

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ABSTRACT

Using the experimental technique of Raman and Venkataraman for the determination of the adiabatic piezo-optic coefficients of liquids, the adiabatic piezo-optic coefficients of three acetates and cyclohexanol have been determined. The temperature variation of refractive index of the above liquids has also been studied using a Pulfrich refractometer. The data obtained for the above four liquids have been discussed in the light of deviations from refraction formulæ, temperature coefficient of refractive index at constant density and the relation between the adiabatic and the isothermal piezo-optic coefficients.

1. INTRODUCTION

The change of refractive index of liquids with pressure has been the subject of several investigations, though most of them concern the change under isothermal conditions. For small values of this applied pressure, *i.e.*, upto say one atmosphere, the resulting changes in refractive index are so small that interferometric methods alone lead to accurate results. It is therefore not surprising to find that Jamin (1857-58) with the refractometer designed by him was the first to undertake such studies. Subsequently Mascart (1874), Röntgen and Zehnder (1891), Himstedt and Wertheimer (1922), Eisele (1925) and a few others have carried out investigations on the isothermal piezo-optic coefficients of liquids and among these the most extensive is that of Röntgen and Zehnder.

The changes in refractive index at high pressures have also been investigated and a dependence of $\frac{dn}{dp}$ on pressure p sought for. Important work in this field has been done by Rosen (1949), Poindexter (1935), Poindexter and Rosen (1934), Gibson and Kincaid (1938) and Poulter, Ritchy and Benz (1932).

The studies mentioned above being of an isothermal nature are necessarily slow, due to the fact that the heat of compression must be allowed to pass away and also the pressure has to be applied slowly by small steps. It has been pointed out by Tyrer (1913-14) in the determination of the isothermal compressibilities of liquids, that the latent heat evolved due to the contraction of the liquid due to a small change of volume is so small that it takes a long time for it to pass away and in fact it is extremely difficult to bring the liquid back to the original temperature. It is therefore obvious that the adiabatic coefficient can be determined much more easily and with a higher accuracy. The calculation of adiabatic coefficient from the isothermal coefficient is also not an easy matter. We also find that it is the adiabatic coefficient which is involved in several optical problems such as the diffraction of light by ultrasonic waves, the diffusion of light due to Debye waves in liquids and so on. Raman and Venkataraman (1939) were the first to make such measurements. They have determined the adiabatic piezo-optic coefficients of 11 liquids including a group of alcohols.

The present investigations were started from where Raman and Venkataraman (*loc. cit.*) had left off and an interferometric measurement of the adiabatic piezo-optic coefficients of three acetates and cyclohexanol has been made. The results have been discussed in the light of deviations from refraction formulæ, change in refractive index with temperature at constant density, etc.

Due to the ambiguity in the values of $\frac{dn}{dt}$ available in the literature a necessity for determining the same was felt. Accordingly the temperature variations of the refractive indices of the above liquids have also been included in this paper.

2. EXPERIMENTAL DETAILS

Owing to its sensitiveness the interferometric technique has been employed widely for the determination of the piezo-optic coefficients. Even a small pressure shifts the interference fringe system appreciably and this enables one to make accurate measurements. even when the external pressures applied are small.

In their experiments. Röntgen and Zehnder. and others used two long parallel metal tubes joined along their length. and also joined at their ends by optically worked glass plates. The pressure was applied with the help of a mercury manometer. The resulting refractive index changes were measured with a Jamin's interferometer after taking adequate precautions to ensure isothermal conditions of measurements. On the other hand. Raman and Venkataraman used the Rayleigh refractometer with the 1 metre cell filled with the liquid for the determination of the adiabatic piezo-optic coefficients. The pressure was applied from a mercury manometer. The instantaneous application and removal of the pressure was effected with the help of a three-way stopcock introduced between the cell and the manometer.

The apparatus used in the present investigation consisted of the same Rayleigh refractometer but with a newly constructed pressure applying arrangement, and a separate manometer was incorporated in the new design to improve the accuracy of the measurements. A schematic diagram of this pressure applying system is shown in Fig. 1. Care was taken to see that the mercury remained clean and did not stick to the glass walls of the manometer.

A water-bath was arranged inside the interferometer so as to keep the interferometer cells at a certain temperature and also for steadying the fringes. Opti-

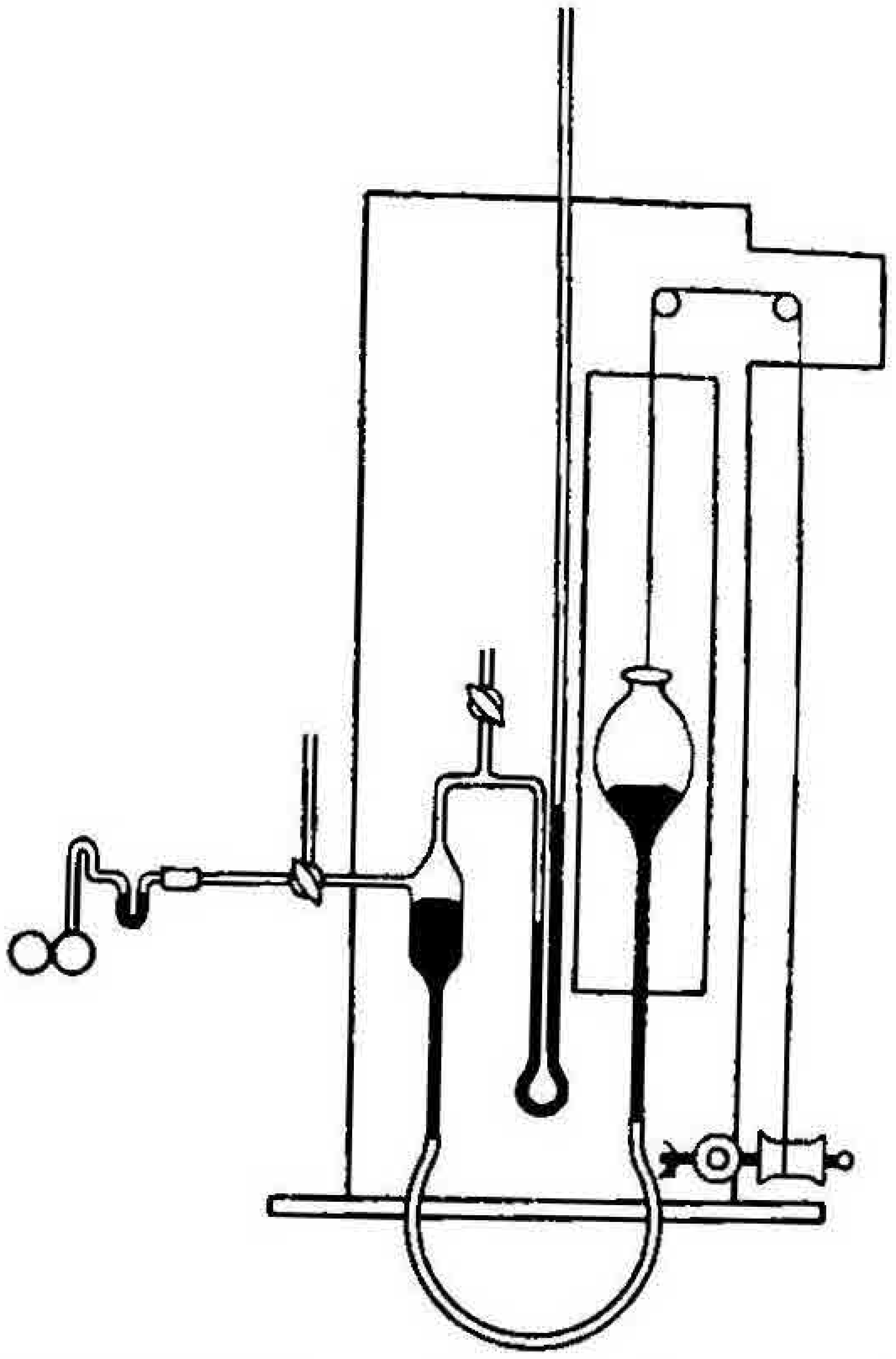

FIG. 1. Arrangement for the application of pressure to the liquid.

cally plane Pyrex glass plates were used as the end windows. The interferometer was set up inside a specially selected dark room which had minimum temperature fluctuation. In addition the measurements were carried out during that part of the day when the temperature did not fluctuate rapidly.

The interferometric cells were cleaned with alcohol and dried by connecting them to a vacuum pump. Then it was filled with the liquid after being twice rinsed. To prevent the contact of liquid in the cell, with the water in the pressure applying system, the small U-tube fused to one of the two tubes of the cell was filled with mercury. The cell was inserted into the bath and clamped in position with the help of two sliding platforms and four screws attached to the water-bath. The cell was then connected to the manometer. The farther ends of the tubes of the cell were stoppered tightly. The whole system was left to itself for sometime for attaining temperature equilibrium.

The source of light used was a Philips sodium lamp with an outer jacket which prevented undue heating of the instrument. The light was passed through a cell of alum solution which absorbed the heat rays and then condensed by a lens on to the slit of the collimator. A clear system of fringes was obtained by adjusting the cell inside the water-bath.

The movable limb of the pressure changing system was raised and the pressure applied to the liquid inside the cell by quickly opening the three-way stopcock. The shift in the number of fringes of the upper system with respect to the stationary ower system being noted, the stopcock was immediately closed putting the cell in contact with the atmosphere. The pressure necessary for shifting an integral number of fringes was obtained from the readings of the levels of the manometer. The readings were made using a cathetometer. This pressure was slightly increased and then decreased so that a deviation from an integral fringe shift was just visible. The mean pressure was thus recorded. This was taken as the mean value of the pressure for shifting a certain integral number of fringes. A correction due to the change in water level in the fixed limb after the application of the pressure was also applied. This correction was found to depend on the pressure applied. The correction for a pressure of 1 cm. of mercury was found and the correction for a certain pressure computed therefrom.

The temperatures near the manometer and the water-bath were recorded at intervals. The temperature of water-bath was constant throughout and a change of ·4° C. was observed near the manometer. The temperature of the water-bath was always less than the temperature near the manometer. The mean temperature near the manometer was used for correcting the pressure obtained to 0° C., sea-level and 45° latitude.

Supposing L be the length of the cell, N the number of fringes shifting due to the application of a pressure p and λ is the wavelength of light used then $\left(\frac{dn}{dp}\right)_\phi$ is given by $N\lambda/Lp$, where $\left(\frac{dn}{dp}\right)_\phi$ is the adiabatic piezo-optic coefficient. The change in refractive index due to the application of 1 atmospheric pressure under standard conditions will be $\left(\frac{dn}{dp}\right)_\phi = (N\lambda/Lp_0)\times 76$, where p_0 is the corrected pressure to 0° C. sea-level and 45° latitude.

Since an analysis of the $(dn/dp)_\phi$ values in terms of the theoretical predictions of Lorentz-Lorenz refraction formula needs an accurate knowledge of the temperature dependence of the refractive index and as such accurate values are not available in literature an experimental study of the variation of n with temperature was made with a Pulfrich refractometer in the range of temperature 20 to 50° C. Temperature regulation was attained by the use of a Gallenkamp water thermostat with a 1000 watts heater fed from a 0–260 variac. Temperature corrections for the readings of the instrument were also applied.

3. RESULTS AND DISCUSSION

In the present study a set of three acetates and a viscous liquid cyclohexanol are considered. Cyclohexanol was distilled twice under vacuum to ensure purity. Methyl and Amyl acetates were pure reagents. Ethyl acetate was prepared and purified by the Organic Chemistry Department.* The purity was checked by the determination of the refractive index of the liquids and comparing the results with that given in the literature.

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Since the method of determining the mean value of the pressure has been described by Venkataraman (1939) only the final values for the liquids are given in Tables I, II, III and IV.

TABLE I. *Ethyl Acetate at 24·2° C.*

Fringes	Mean pressure	Final corrected pressure	Adiabatic piezo-optic coefficient
1	1·987	1·973	22·70
2	3·976	3·949	22·69
3	5·966	5·925	22·68
4	7·979	7·924	22·61
5	9·948	9·880	22·67
6	11·933	11·851	22·68
7	13·928	13·832	22·67

Mean (22·67 ± ·01) × 10^{-6}

TABLE II. *Methyl Acetate at 24·6° C.*

Fringes	Mean pressure	Final corrected pressure	Adiabatic piezo-optic coefficient
1	1·533	1·522	29·43
2	3·060	3·039	29·47
3	4·612	4·580	29·34
4	6·171	6·128	29·23
5	7·698	7·644	29·30
6	9·163	9·099	29·53
7	10·674	10·599	29·58
8	12·186	12·101	29·61
9	13·798	13·701	29·42
10	15·396	15·288	29·30

Mean (29·42 ± ·03) × 10^{-6}

TABLE III. *Amyl Acetate at 24·2°C.*

Fringes	Mean pressure	Final corrected pressure	Adiabatic piezo-optic coefficient
1	1·732	1·720	25·99
2	3·471	3·447	26·07
3	5·190	5·154	26·04
4	6·886	6·839	26·20
5	8·650	8·590	26·07
6	10·464	10·392	25·86
7	12·162	12·078	25·96
8	13·931	13·835	25·90
9	15·637	15·529	25·96

Mean (26·01 ± ·02) ×10^{-6}

TABLE IV. *Cyclohexanol at 23° C.*

Fringes	Mean pressure	Final corrected pressure	Adiabatic piezo-optic coefficient
1	1·983	1·970	22·73
2	3·950	3·924	22·83
3	5·949	5·909	22·74
4	7·883	7·830	22·87
5	9·864	9·798	25·86
6	11·859	11·780	22·81
7	13·853	13·761	22·78
8	15·914	15·808	22·67
9	17·933	17·814	22·63

Mean (22·77 ± ·02)×10^{-6}

The temperatures and the corresponding indices of refraction for the wavelength 5893 Å of Sodium are tabulated in Tables V, VI, VII and VIII. In the temperature range studied the graph connecting the temperature and the refractive index was found to be a straight line in the case of all the above liquids. By the method of least squares equations of the form $n_t = n_0 + bt$ were fitted to the values obtained for the refractive indices at different temperatures.

TABLE V. *Ethyl Acetate*

Temp. °C.	*n* obs.	*n* calcd.
22·7	1·37091	1·37091
23·7	042	045
25·8	1·36950	1·36950
27·7	865	864
32·1	667	664
38·1	390	392

$n_t = 1{\cdot}41066 - 43{\cdot}58 \times 10^{-5} \times t$

TABLE VI. *Methyl Acetate*

Temp. °C.	*n* obs.	*n* calcd.
22·2	1·35603	1·35601
23·0	572	568
26·4	434	426
30·6	242	252
33·85	108	117
34·6	075	085
38·25	1·34931	1·34934
42·2	784	779

$n_t = 1{\cdot}47156 - 37{\cdot}43 \times 10^{-5} \times t$

TABLE VII. *Amyl Acetate*

Temp. °C.	*n* obs.	*n* calcd.
22·7	1·40075	1·40077
25·3	1·39960	1·39963
28·3	832	828
33·3	620	615
33·8	595	593
39·0	361	366

$n_t = 1{\cdot}38120 - 45{\cdot}35 \times 10^{-5} \times t$

TABLE VIII. *Cyclohexanol*

Temp. °C.	*n* obs.	*n* calcd.
22·8	1·46301	1·46303
24·1	254	254
25·7	198	194
30·0	030	033
36·5	1·45791	1·45789
43·2	547	539
47·4	376	382

$n_t = 1{\cdot}36524 - 41{\cdot}58 \times 10^{-5} \times t$

For a discussion of the results in addition to the temperature coefficient of refractive index, an accurate knowledge of the adiabatic and isothermal compressibilities at the temperature at which the piezo-optic coefficient is determined, the specific heat at constant pressure and the thermal dilatation of the liquids are necessary. The available data for the above have been collected and mean of the reliable values are used wherever possible. The data for α the cubical expansion have been calculated from the equations connecting volume and temperature, and density and temperature. The density temperature relations are taken from the *International Critical Tables* and the *Landolt-Bornstein Tabellen.* The values taken from the latter agree well with the calculated values. The values of C_p have been taken from the results of various authors. Table IX gives the data collected for the various liquids studied.

TABLE IX

Data for the Liquids Studied

Liquid	Formula	Temp. °C.	n author	$\frac{dn}{dt} \times 10^5$ author	$\alpha \times 10^5$	C_p	$\beta_t \times 10^6$	$\beta_\phi \times 10^6$	$\left(\frac{dn}{dp}\right)_\phi \times 10^6$	$\left(\frac{dn}{dp}\right)_t \times 10^6$ calcd.
Ethyl acetate	$CH_3COOC_2H_5$	24·2	1·3702	−45·35	134·7	·4632	119	87	22·67	33·21
Methyl acetate	CH_3COOCH_3	24·6	1·3550	−41·58	140·3	·4633	116	82·7	29·42	39·43
Amyl acetate	$CH_3COO(CH_2)_4CH_3$	24·2	1·4001	−43·58	115·4	..	..	..	26·01	..
Cyclo-hexanol	$C_6H_{11}OH$	23·0	1·4630	−37·43	81·4	·5011	58·3	49·6	22·77	26·78

In the case of Cyclohexanol, the isothermal compressibility was calculated from the value of the adiabatic compressibility known from the sound velocity measurements. Knowing the value of C_p the specific heat at constant pressure, α the cubical expansion, T the absolute temperature, J the mechanical equivalent of heat and ρ the density at a temperature T, β_t was calculated from β using the thermodynamical relation

$$\beta_t - \beta_\phi = \frac{1 \cdot 013 \times 10^6 \times T \times \alpha^2}{J \times C_p \times \rho}$$

J the mechanical equivalent of heat was taken to be equal to $4 \cdot 186 \times 10^7$ ergs per calorie.

Elasto-optic and Piezo-optic coefficients.—According as the variation in the refractive index on the application of pressure is regarded in terms of the applied pressure or the consequent change in density we have the piezo-optic or the elasto-optic coefficient.

For the adiabatic process we have therefore

$$\left(\frac{dn}{dp}\right)_\phi = \left(\frac{dn}{d\rho}\right)_\phi \left(\frac{d\rho}{dp}\right)_\phi = \left(\frac{dn}{d\rho}\right)_\phi \beta_\phi \rho$$

Similarly for the isothermal process we have

$$\left(\frac{dn}{dp}\right)_t = \rho \left(\frac{dn}{d\rho}\right)_t \beta_t$$

The ratio of the two coefficients (piezo-optic) is not equal to the ratio of the corresponding compressibilities due to a finite difference between the two elasto-optic coefficients on account of the existence of a pure temperature effect on the refractive index and also because there is a very small rise of temperature during adiabatic compression (Raman and Venkataraman, *loc. cit.*). This difference is given by

$$\rho \left(\frac{dn}{d\rho}\right)_\phi - \rho \left(\frac{dn}{d\rho}\right)_t = \left(\frac{dn}{dt}\right)_\rho \left(\frac{dt}{dp}\right)_\phi \beta_\phi .$$

Expressed in terms of the piezo-optic coefficients this becomes

$$\left(\frac{dn}{dp}\right)_\phi = \left(\frac{dn}{dp}\right)_t \frac{\beta_\phi}{\beta_t} + \left(\frac{dn}{dt}\right)_\rho \left(\frac{dt}{dp}\right)_\phi$$

The isothermal piezo-optic coefficients have been calculated for the above liquids. For want of data it has not been possible to calculate the isothermal piezo-optic coefficient for amyl acetate.

On the basis of the Lorenz-Lorentz and other refraction formulæ one can obtain expressions for the elasto-optic coefficients by differentiation. Since the basis of the Lorenz-Lorentz formula is that n is a function of density alone we find that $\rho \frac{dn}{d\rho}$ should be the same whether for a change in density due to change of temperature at constant pressure, or due to variation of pressure at constant temperature or constant entropy.

Hence

$$-\frac{1}{\alpha}\left(\frac{dn}{dt}\right)_p = \frac{1}{\beta_\phi}\left(\frac{dn}{dp}\right)_\phi = \frac{1}{\beta_t}\left(\frac{dn}{dp}\right)_t = \rho \left(\frac{dn}{d\rho}\right)_{\text{Lorentz}}$$

and

$$\rho \left(\frac{dn}{d\rho}\right)_{\text{Lorentz}} = \frac{(n^2-1)(n^2+2)}{6n}$$

As found by Raman and Venkataraman the values calculated from the Lorenz-Lorentz equation are always higher than the measured values of the change in refractive index for pressure changes. The experimentally measured values of $-\frac{1}{\alpha}\left(\frac{dn}{dt}\right)_p$ are also less than the values from the Lorenz-Lorentz formula.

Further one can notice that except for Methyl acetate the values of $-\frac{1}{\alpha}\left(\frac{dn}{dt}\right)_p$ are numerically greater than either the adiabatic or isothermal values of $\frac{1}{\beta}\left(\frac{dn}{dp}\right)$. In view of the fact that in the case of crystals a refraction formula of the type $n^2 - 1 = \text{constant} \times \rho$ explains their optical behaviour, the calculated values on the basis of refractivity equations have also been included in Table X. Formula $n^2 - 1 = \text{constant} \times \rho$ gives reasonable values for Ethyl acetate whereas Gladstone and Dale relation leads to better results in the case of Cyclohexanol. It is interesting to note that cyclohexanol which can be expected to show some association has nearly the same value for

$$-\frac{1}{\alpha}\left(\frac{dn}{dt}\right)_p, \quad \frac{1}{\beta_\phi}\left(\frac{dn}{dp}\right)_\phi$$

and

$$\frac{1}{\beta_t}\left(\frac{dn}{dp}\right)_t$$

although all of them differ much from the value given by Lorenz-Lorentz formula.

According to Raman and Venkataraman the difference between $\frac{1}{\beta_t}\left(\frac{dn}{dp}\right)$ and that given by Lorenz-Lorentz formula should be entirely due to the polarisation field alone.

TABLE X

Deviations from Refractivity Formulæ

Liquid	Temp. °C.	A	B	C	D	E	F	G
Ethyl acetate	24·2	·3367	·2603	·4138	·3202	·3702	·3909	·2793
Methyl acetate	24·6	·2964	·3557	·3945	·3085	·3550	·3743	·3720
Amyl acetate	24·2	·3776	..	·4527	·3429	·4001	·4236	..
Cyclohexanol	23·0	·4598	·4591	·5379	·3897	·4630	·4928	·4595

Note: $A = -\frac{1}{\alpha}\left(\frac{dn}{dt}\right)_p$; $B = \frac{1}{\beta_\phi}\left(\frac{dn}{dp}\right)_\phi$; $C = \frac{(n^2-1)(n^2+2)}{6n}$; $D = \frac{n^2-1}{2n}$; $F = n-1$;

$F = \frac{(n^2-1)(n+\cdot 4)}{(n^2+\cdot 8n+1)}$ and $G = \frac{1}{\beta_t}\left(\frac{dn}{dp}\right)_t$ (calculated).

Temperature variation of refractive index at constant density.—The pure temperature effect namely the change in refractive index with temperature alone may be evaluated by comparing the variation of refractive index with temperature at constant pressure with the change produced by isothermal or adiabatic compression. These are given by

$$\left(\frac{dn}{dt}\right)_\rho = \left[\alpha\left(\frac{dn}{dp}\right)_t + \beta_t\left(\frac{dn}{dt}\right)_p\right] \Big/ \beta_t$$

and

$$\left(\frac{dn}{dt}\right)_\rho = \left[\alpha\left(\frac{dn}{dp}\right)_\phi + \beta_\phi\left(\frac{dn}{dt}\right)_p\right] \Big/ \left[\alpha\left(\frac{dn}{dp}\right)_\phi + \beta_\phi\right]$$

These can also be written as

$$\left(\frac{dn}{dt}\right)_\rho = \alpha\left[\rho\left(\frac{dn}{d\rho}\right)_t - \rho\left(\frac{dn}{d\rho}\right)_p\right]$$

and

$$\left(\frac{dn}{dt}\right)_\rho = \left[\rho\left(\frac{dn}{d\rho}\right)_\phi - \rho\left(\frac{dn}{d\rho}\right)_p\right] \Big/ \left[\frac{1}{\alpha} + \left(\frac{dt}{dp}\right)_\phi \Big/ \beta_\phi\right]$$

where $\left(\frac{dt}{dp}\right)_\phi$ is the small change in temperature due to the adiabatic compression by one atmospheric pressure and is given by

$$\left(\frac{dt}{dp}\right)_\phi = \frac{T\alpha}{JC_p}\, 1\cdot01325 \times 10^6$$

Table XI contains the values of the temperature variation of the refractive index at constant density calculated from the above using the values of the adiabatic piezo-optic coefficients.

TABLE XI

Temperature Variation of Refractive Index at Constant Density

Liquid	Temp. °C.	$\left(\frac{dn}{dt}\right)_\rho \times 10^5$	$\left(\frac{dn}{dt}\right)_{\text{absolute}}$	$\left(\frac{dn}{dt}\right)_p \times 10^5$ obs.
Ethyl acetate ..	24·2	−7·8	−37·55	−45·35
Methyl acetate ..	24·6	+6·1	−47·68	−41·58
Amyl acetate ..	24·2	..	..	−43·50
Cyclohexanol ..	23·0	−0·1	−37·33	−37·43

In agreement with what has been stated earlier we find that Ethyl acetate which shows large deviations from Lorenz-Lorentz refraction formula has large pure temperature coefficient.

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5. REFERENCES

1. Bhagavantam and Joga Rao *Proc. Ind. Acad. Sci.*, 1939, **9**, 312.
2. Chang .. *Chinese J. Phys.*, 1935, **1** (2), 1.
3. Danforth .. *Ind. Eng. Chem. Anal.*, 1938, **10**, 559.
4. Eisele .. *Ann. Phys. Chem.*, 1925, **76**, 396.
5. Gibson and Kincaid .. *J. Am. Chem. Soc.*, 1938, **60**, 511.
6. Grassi .. *Ann. Phys. Chem.*, 1851, **31**, 437.
7. Himstedt and Werteimer .. *Ibid.*, 1922, **67**, 395.
8. Jamin .. *Compt. Rend.*, 1857, **45**, 892.
   Ann. Chem. Phys., 1858, **52**, 165.
9. Mascart .. *Pogg. Ann.*, 1874, **153**, 154.
   Compt. Rend., 1874, **78**, 617.
   Ibid., 1874, **78**, 801.
10. Partington, J. R. .. *Advanced Treatise on Physical Chemistry*, Vol. IV.
11. Poindexter .. *Phys. Rev.*, 1935, **47**, 202.
12. ——— and Rosen .. *Ibid.*, 1934, **45**, 760.
13. Poulter, Ritchy and Benz .. *Ibid.*, 1932, **41**, 366.
14. Quincke .. *Ann. Phys. Chem.*, 1883, **19**, 401.
15. Raman and Venkataraman *Proc. Roy. Soc. London*, 1939, **171**, 137.
16. Rontgen and Zehnder .. *Ann. Der. Phys. Chem.*, 1891, **44**, 24.
17. Rosen .. *J. Chem. Phys.*, 1949, **17**, 1192.
18. Shiba .. *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, 1931, **16**, 205.
19. Tilton .. *J. Res. Natl. Bur. Stands.*, 1935, **14**, 393.
20. Tyrer .. *Z. Phys. Chem.*, 1914, **87**, 169.
    J. Chem. Soc., 1913, **103**, 1675.
    Ibid., 1914, **105**, 2534.
21. Venkataraman .. *Proc. Ind. Acad. Sci.*, 1939, **10**, 121.
22. Zehnder .. *Ann. Phys. Chem.*, 1888, **34**, 91.
    Z. Phys. Chem., 1888, **2**, 111.