168. *The Refractivity of Formamide.*

By Gilbert F. Smith.

Measurements have been made of the refractive indices of formamide at 20° for twenty wave-lengths in the visible spectrum. The refractive dispersion can be represented by a simplified Ketteler–Helmholtz dispersion formula containing one variable term, but it is unlikely that this equation will apply unchanged to other regions of the spectrum.

When a pure specimen of formamide was first obtained (Smith, J., 1931, 3257) it seemed desirable to measure certain of its physical properties, among these being refractivity. At this time there had been developed in Cambridge a new and highly accurate technique for the determination of refractive indices, and the late Professor T. M. Lowry kindly placed his apparatus at the author's disposal. A number of measurements were therefore made in both the visible and the ultra-violet region of the spectrum, and although it has not been possible to complete those in the latter region, the results in the visible are now recorded.

In the table are given the data for 20 wave-lengths from 6708 to 4358 A., thus covering practically the whole range over which visual observations are possible. The refractive indices (col. 2) were measured with an improved Pulfrich refractometer, which had been calibrated against quartz for 30 wave-lengths (Lowry and Allsopp, *Proc. Roy. Soc.*, 1931, *A*, **133**, 26). The accuracy of the determinations is about one unit in the fourth decimal place, although an additional figure is included in the table.

The Refractivity of Formamide (*m. p.* 2·55°).

λ.	$n_{20°}$, obs.	$n_{20°}$, calc.	Diff. $\times 10^4$.	$[R_L]_\lambda$.	λ.	$n_{20°}$, obs.	$n_{20°}$, calc.	Diff. $\times 10^4$.	$[R_L]_\lambda$.
Li 6707·86	1·44367	1·44394	−2·7	10·550	Cu 5220·06	1·45223	1·45210	+1·3	10·726
Zn 6362·34	1·44518	1·44525	−0·7	10·581	Cu 5105·55	1·45331	1·45309	+2·2	10·748
Li 6103·6	1·44641	1·44643	−0·2	10·606	Ba 4934·10	1·45501	1·45474	+2·7	10·783
Na 5895·93	1·44754	1·44750	+0·4	10·629	Zn 4810·53	1·45602	1·45606	−0·4	10·803
Hg 5790·66	1·44817	1·44810	+0·7	10·642	Cd 4799·91	1·45624	1·45619	+0·5	10·808
Cu 5782·15	1·44815	1·44816	−0·1	10·642	Zn 4722·16	1·45714	1·45709	+0·5	10·826
Cu 5700·24	1·44849	1·44865	−1·6	10·649	Cd 4678·15	1·45769	1·45759	+1·0	10·837
Ba 5535·5	1·44983	1·44972	+1·1	10·676	Li 4603·0	1·45879	1·45894	−1·5	10·860
Ag 5471·51	1·45011	1·45020	−0·9	10·682	Ba 4554·04	1·45933	1·45923	+1·0	10·871
Hg 5460·73	1·45028	1·45024	+0·4	10·685	Hg 4358·34	1·46211	1·46215	−0·4	10·928

As might be expected, the refractive dispersion of formamide can be represented by a simplified Ketteler–Helmholtz dispersion formula containing one variable term. The most satisfactory equation was found to be $n^2 = 1{\cdot}63709 + 0{\cdot}41561\lambda^2/(\lambda^2 - 0{\cdot}03230)$, where λ is expressed in μ. The figures in col. 3 show that this equation can reproduce the experimental dispersion curve with some accuracy, although there are indications of systematic deviations in the region of wave-lengths 4934—5220 A. The equation predicts a characteristic vibration frequency for the formamide molecule in the extreme ultra-violet, corresponding to a wave-length λ_0 of about 1800 A. This suggests that the equation is unlikely to be valid outside the range of the visible spectrum, and that additional terms will probably have to be added before it can be applied to the ultra-violet, for it has usually been found (Lowry and Allsopp, *loc. cit.*; Allsopp and Willis, *ibid.*, 1936, *A*, **153**, 379) that it is only when the characteristic frequency lies in the far Schumann region that the dispersion in both the visible and the ultra-violet can be represented by an equation containing a single variable term.

Included in the table are values for the molecular refractivity, calculated from the Lorentz–Lorenz formula $[R_L] = (n^2 - 1)M/(n^2 + 2)d$, the density of formamide being taken as 1·13339 at 20° (Smith, *loc. cit.*). Previous determinations of the refractive indices for five different wave-lengths were made by Brühl (*Z. physikal. Chem.*, 1895, **16**, 193) and by Schmidt (*ibid.*, 1907, **58**, 522). Brühl gave $[R_L]_D = 10{\cdot}59$, and Schmidt gave 10·56. Both of these are appreciably lower than the present value of 10·629. Schmidt also gave 1·44341 as the refractive index for the red lithium line at 20°; this differs by less than three units in the fourth place from the present value, which is somewhat surprising since his sample of formamide appears to have been seriously contaminated, for it had *d* 1·1394, which is over 0·5% too high.

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