[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, COLLEGE OF ENGINEERING, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Infrared Absorption of Liquid and Gaseous 1,4-Dioxane between 1.4 and 14.0 μ

BY D. S. MCKINNEY, C. E. LEBERKNIGHT AND J. C. WARNER

The infrared absorption of liquid and gaseous dioxane has been investigated between 1.4 and 14.0 μ using a rock salt spectrometer. The region from 2.27 to 3.72 μ also has been studied using a prism-grating spectrometer. The 1,4-dioxane was purified by refluxing over metallic sodium using a 24-inch (61-cm.) fractionating column packed with short pieces of glass tubing. The fraction used boiled at 99.3–99.4° at 738 mm.

The rock salt spectrometer consists of an equilateral prism 8.5 cm. on an edge so arranged as to pass the energy through the prism twice, thus securing a high resolving power without the necessity of using extremely narrow slits. Effective slit widths for various spectral regions are as follows

Region (μ)	4	7	12	14
Effective slit (μ)	0.01	0.01	0.02	0.06

Effective slit widths, in wave numbers, are given in Figs. 1 and 2. The existing data on the dispersion of rock salt were not considered accurate enough for the calibration of the instrument. It was therefore necessary to select suitable materials for calibration. The following established bands and lines were used:

Sodium D lines (mean)	0.5893 μ		
Benzene band at	2.464 μ		
Q branches of ethylene bands at	5.292 μ	6.925 μ	10.53 μ

The data of Cross[1] were used to interpolate between the calibration points. It has been found possible to resolve the above ethylene bands practically as well as done by Levin and Meyer[2] using grating instruments. The spectrometer is enclosed in a steel case. The thermocouple, its leads and the galvanometer, are also shielded in steel pipe. The shielding and spectrometer are grounded. The steel spectrometer case is covered with a Masonite case to prevent local changes in temperature.

The grating instrument consisted of an echelette grating with a resolving power of 15,000 in the first order and a small angle rock salt prism which was used to eliminate lower order energy. The energy was measured by means of compensating single-junction vacuum thermocouples connected to a Leeds and Northrup high voltage sensitivity galvanometer. The deflections of this galvanometer were amplified by means of an optical relay. The calculations of Firestone[3] concerning the relation between the speed of response and resistance of the thermocouple were confirmed. Due to external disturbances, extreme care had to be taken to ensure stability in the receiving system. The unique features of the rock salt spectrometer and the receiving system will be published elsewhere. This report will describe in detail the means of ensuring stability even when operating near the limit of sensitivity fixed by the Brownian motion of the first galvanometer.

A survey of the spectrum of liquid dioxane from 1.4 to 14.0 μ (Fig. 1, top) using a 0.2-mm. cell showed four regions of intense absorption at 880, 1100, 1350 and 2800 cm.$^{-1}$, and regions of moderate absorption at 1720, 1950, 3550 and 4200 cm.$^{-1}$. The regions of intense absorption were first studied using 0.02-mm. cells (marked C, Fig. 1). The correct thickness in these cells was obtained by rolling lead sheet to the desired thickness and cutting washers from the lead ribbon which were used as spacers between the rock salt windows. In the regions around 880, 1100, 1350 and 2800 cm.$^{-1}$ absorption was still intense with the 0.02-mm. cell. These regions were therefore investigated using a cell in which the windows were pressed together with only a capillary film of dioxane between (curves marked B, Fig. 1). With this cell there was still almost complete absorption in the regions of 880 and 1100 cm.$^{-1}$. These regions were finally studied using a cell made up of carefully polished flat rock salt windows, held together by small spring clips (curves marked A, Fig. 1). Since the wave number resolving power of the prism instrument is rather poor at shorter wave lengths than 4 μ, the regions of wave number 2800 cm.$^{-1}$ and greater were studied in detail on the prism grating spectrometer. The effective slit widths, in wave numbers, for the various spectral regions, are marked in Figs. 1 and 2. The regions 880,

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[1] Cross, *Rev. Sci. Instruments*, **4**, 197 (1933).

[2] Levin and Meyer, *J. Optical Soc. Am. and Rev. Sci. Inst.*, **16**, 137 (1928).

[3] Firestone, *Rev. Sci. Instruments*, **1**, 630 (1930).

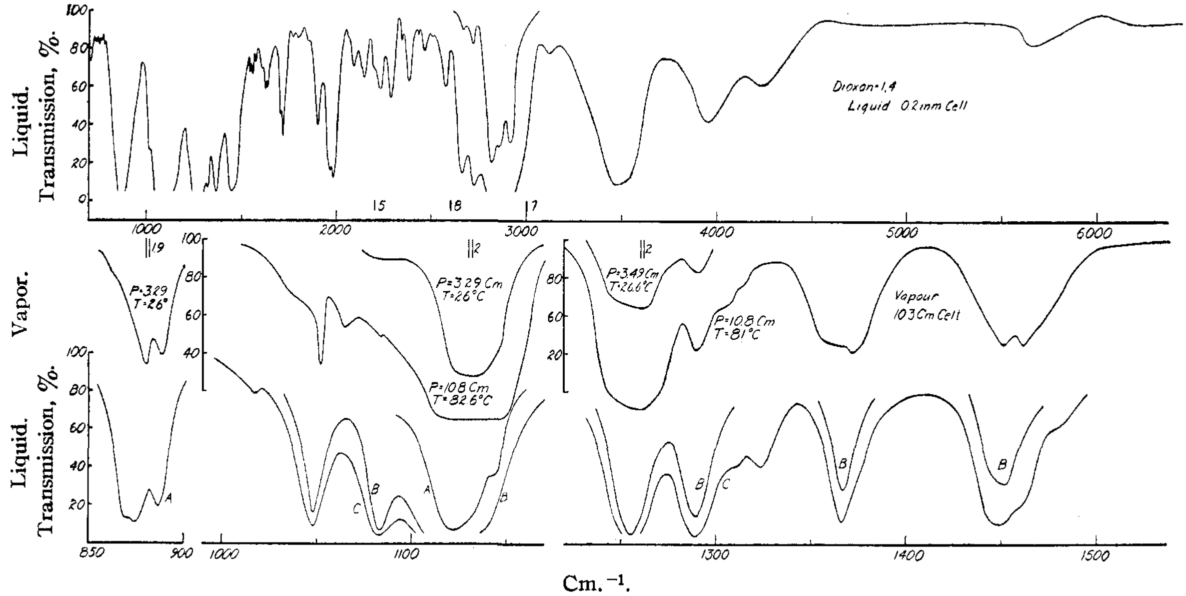

Fig. 1.—Liquid: A, very thin cell; B, moderately thin cell; C, 0.02-mm. cell.

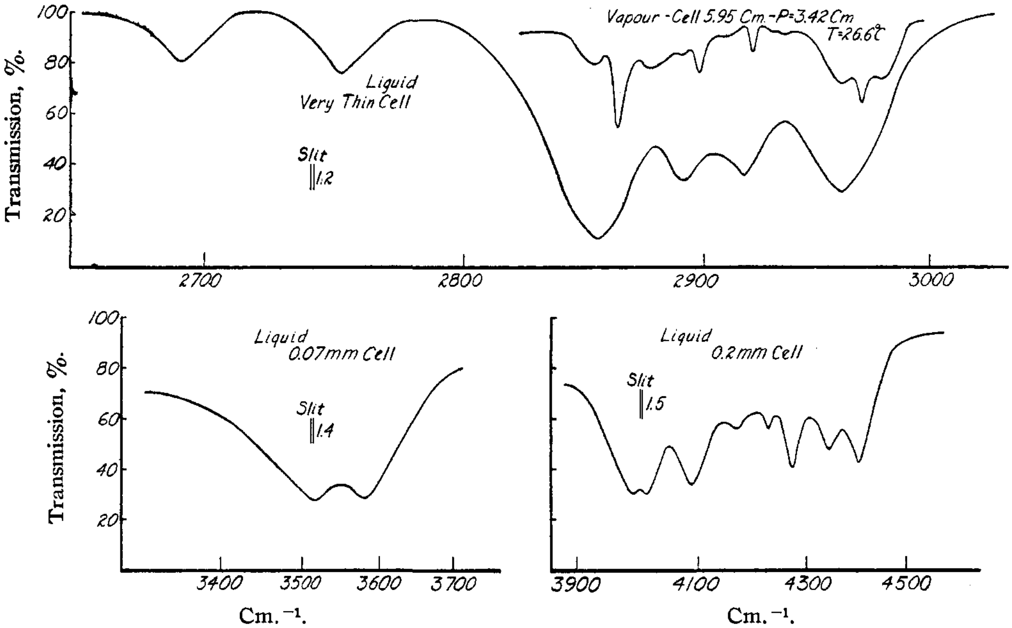

Fig. 2.

1100 and 1350 cm.$^{-1}$, using thin liquid cells, are shown to a larger scale in the lower part of Fig. 1. Each region is seen to be composed of a number of bands (3 in 880, 5 in 1100 and at least 5 in 1350 cm.$^{-1}$ region).

The absorption of gaseous dioxane was next investigated in a 10.3-cm. cell with rock salt windows containing dioxane vapor. To guard against the condensation of liquid dioxane on the windows, the cell was filled with a mixture of 20% dry air and 80% dry air saturated with dioxane vapor. With this concentration of dioxane only the more intense bands were observed. To secure higher concentration without increasing the cell length, a cell was made with a small bulb sealed to one side containing liquid dioxane. This cell and side bulb were heated electrically, always maintaining the cell at a higher temperature than the side bulb. The temperature of the bulb determines the vapor pressure of dioxane in the cell, while the higher temperature of the cell prevents condensation on the windows. The dioxane pressures (in cm.) and the cell temperatures are recorded on Figs. 1 and 2.

Comparison with the vapor shows that the bands are not markedly different from the liquid, the shift in the location of the bands is toward higher frequencies in the vapor and is not constant for the various components. The vapor band at 1050 cm.$^{-1}$ shows evidence of rotation (envelope of vibration–rotation band).

The regions at 2880, 3550 and 4200, cm.$^{-1}$ were studied with the grating spectrometer (Fig. 2). At 2880, 6 bands were found in the liquid. Of these the four most intense were studied in the vapor, where again the envelope of the vibration–rotation bands is clear. The shifts for these bands are again unequal:

$\bar{\nu}$ in Liquid	Shift in vapor
2854.9	+8.5
2891.0	+7.1
2916.6	+4.4
2960.8	+8.9

Furthermore, the breadths of the two bands 2855 and 2961 are not the same, the latter being 24 wave numbers (which is the same as that at 1050 cm.$^{-1}$) and the former 34 wave numbers. The bands at 3550 and 4200 wave numbers were studied only in the liquid state. That at 3550 was resolved into a doublet. The 4200 bands show a more complicated structure. Table I shows the positions of the bands studied in detail on the prism spectrometer and comparison with the Raman spectra.[4-6] Table II shows the positions of the bands studied on the grating, and comparison with the Raman Spectra.[4-6] In all 55 bands were found. The comparison with

TABLE I

FREQUENCIES OBSERVED IN THE INFRARED ABSORPTION OF LIQUID AND GASEOUS DIOXANE. SOME FREQUENCIES FROM RAMAN SPECTRUM GIVEN FOR COMPARISON. (WAVE NUMBERS CM.$^{-1}$) PRISM SPECTROMETER

Infrared frequencies			Raman frequencies		
Liquid	Gas		K. and S.[a]	W. and S.[b]	V.[c]
			430 (3)		
			487 (4)		
870 (vs)			833 (9)	836	837
874 (vs)	880				
887 (vs)	889				
1017 (s)			1014 (6)	1017	
1048 (s)	1052				
	1065				
1083 (s)	1084		1107 (3)		
1122 (vs)	1133		1123 (3)	1117	1115
1142 (s)			1215 (4)		
	(mean)	(peak)			
1256 (vs)	1255	1261			
1289 (vs)	1290		1303 (7)		
1322 (s)			1333 (0)	1306	
	(mean)	(peak)			
1367 (s)	1367	1371			
1452 (s)	1451		1442 (6)	1450	1442
	1461		1460 (2)		
1543 (w)					
1558 (w)					
1574 (w)					
1610 (w)					
1624 (w)					
1636 (w)					
1703 (m)					
1717 (m)					
1771 (w)					
1797 (w)					
1855 (w)					
1899 (m)					
1964 (m)					
1982 (m)					
2087 (w)					
2143 (w)					
2234 (w)					
2286 (w)					
2344 (w)					
2380 (w)					
2433 (w)					
2502 (w)					
2575 (w)					

(vs) very strong
(s) strong
(m) moderate
(w) weak

[a] K. and S., Kohlrausch and Stockmair, *Z. physik. Chem.*, **B31**, 382 (1936).

[b] W. and S., Wolkenstein and Syrkin, *J. Chem. Phys.*, **3**, 594 (1935).

[c] V., Villars, THIS JOURNAL, **52**, 4612 (1930).

TABLE II

FREQUENCIES OBSERVED IN THE INFRARED ABSORPTION OF LIQUID AND GASEOUS DIOXANE. SOME FREQUENCIES FROM RAMAN SPECTRUM GIVEN FOR COMPARISON. (WAVE NUMBERS CM.$^{-1}$) PRISM-GRATING SPECTROMETER

Infrared frequencies		Raman frequencies		
Liquid	Gas	K. and S.	W. and S.	V.
2690 (m)		2663 (0)		
2752 (m)		2720 (3)	2720	
2855 (vs)	2863	2854 (8b)	2852	2864
2891 (vs)	2898	2895 (4)		
2917 (vs)	2921			
2961 (vs)	2970	2963 (9b)	2967	2971
3118 (w)		3040 (0)		
3513 (s)				
3582 (s)				
3988,(m)				
4011 (m)				
4085 (m)				
4164 (m)				
4224 (m)				
4272 (m)				
4343 (m)				
4402 (m)				
5652 (w)				
6200 (w)				

(4) Villars, THIS JOURNAL, **52**, 4612 (1930).

(5) Wolkenstein and Syrkin, *J. Chem. Phys.*, **3**, 594 (1935).

(6) Kohlrausch and Stockmair, *Z. physik. Chem.*, **B31**, 382 (1936).

Raman spectra shows good agreement, especially with the results of Kohlrausch and Stockmair. The superior resolving power of the prism spectrometer used in this work is illustrated by comparison with the work of Gordy[7] on dioxane–water mixtures using a fluorite prism spectrometer. In the region 5.9 to 6.5 μ (1695 to 1538 cm.$^{-1}$) Gordy used too thin a cell (0.02 mm.) to detect the six weak bands found by us. In the region from 4.4 to 5.2 μ (2273 to 1923 cm.$^{-1}$) Gordy finds one band at 5.05 μ (1980 cm.$^{-1}$). Our instrument resolves this band into two at 1964 and 1982 cm.$^{-1}$. The single band found by Gordy at 3.38 μ (2959 cm.$^{-1}$) was resolved by our prism instrument into three bands as shown in the curve inserted in Fig. 1 (top). Subsequent examination on the grating spectrometer showed four bands at 2855, 2891, 2917 and 2961 cm.$^{-1}$ (Fig. 1, bottom).

The authors acknowledge with thanks a grant-in-aid from the National Research Council to one of us (J. C. W.), which made possible the construction of the rock salt prism spectrometer.

Summary

The infrared absorption of liquid and gaseous 1,4-dioxane has been investigated between 1.4 and 14.0 μ using a rock salt spectrometer of unusually high resolving power. The region from 2.27 to 3.72 μ has also been investigated using a prism - grating spectrometer. The absorption in the gas is not much different than that observed in the liquid. In passing from the liquid to the gas there is a slight shift to higher frequencies: For example, the liquid bands in the 3.45 μ region are shifted 4 to 9 wave numbers, and the vapor band shape is characteristic of the envelope of vibration–rotation lines.

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(7) Gordy, *J. Chem. Phys.*, **4**, 769 (1936).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Viscosity of Aqueous Solutions of Electrolytes as a Function of the Concentration. V. Sodium Chloride

BY GRINNELL JONES AND SCHUYLER M. CHRISTIAN

This paper gives data on the viscosity of aqueous solutions of sodium chloride at both 25 and 0° from 0.002 up to 2 *N*. The earlier papers[1] of this series should be consulted for a discussion of the historical background and theoretical interest of the problem.

The best measurements at 25° appear to be those of Ruby Kawai;[2] at 18° those of Grüneisen;[3] and at 0° those of Lyle and Hosking.[4] The only measurements at extreme dilution known to us are those of Bousfield[5] at 18° which extend down to 0.0017 *N*.

The best sodium chloride available by purchase was dissolved, filtered through a sintered glass filter, then precipitated in a silica dish by passing hydrochloric acid gas into the solution and dried in a centrifuge. The process, except the filtration, was then repeated and the salt finally dried by ignition to a red heat in a platinum dish. The solutions were made up by weight and the period of flow determined in an Ostwald viscometer, the same instrument used by Jones and Stauffer. The timing was done by the automatic photoelectric cell method developed by Jones and Talley. The results are shown in Tables I and II. The figures for the density are the averages of two or three independent determinations which rarely differed by more than 0.001%, obtained with different pycnometers of approximately 60-ml. capacity.

Unfortunately the density determinations on the 2 *N* solutions were omitted through an oversight, but this figure has been estimated with sufficient precision for the purpose from the data of Baxter and Wallace.[6] The fourth column gives the values of d_ct_c/d_0t_0, which is the average of results obtained with at least two fillings of the viscometer and of several runs on each filling.

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(1) Grinnell Jones and M. Dole, THIS JOURNAL, **51**, 2950 (1929); Grinnell Jones and S. K. Talley, *ibid.*, **55**, 624, 4124 (1933); *Physics*, **4**, 215 (1933); Grinnell Jones and H. J. Fornwalt, THIS JOURNAL, **57**, 2041 (1933); **58**, 619 (1936); Grinnell Jones and R. E. Stauffer, *ibid.*, **58**, 2558 (1936).

(2) C. E. Ruby and J. Kawai, *ibid.*, **48**, 1119 (1926).

(3) E. Grüneisen, *Wiss. Abhandl. physik.-tech. Reichsanstalt*, **4**, 245 (1905).

(4) T. R. Lyle and R. Hosking, *Phil. Mag.*, **3**, 487 (1902).

(5) W. R. Bousfield, *Phil. Trans.*, **206A**, 101 (1906).

(6) G. P. Baxter and C. C. Wallace, THIS JOURNAL, **38**, 83 (1916).