THE OPTICAL ROTATORY POWER OF CANE SUGAR WHEN DISSOLVED IN PYRIDINE

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Since Biot first measured the specific rotation of cane sugar in 1835, many observers have repeated his experiments, and the effects of concentration and temperature, upon the specific rotation have been carefully determined, the former by Tollens,¹ Schmitz, and others; the latter by Andrews, Schönrock, and recently by Pellat.² Naturally, water was the solvent first used; and no others seem to have been employed, probably on account of the difficulty in finding other liquids in which sugar is soluble.

Tollens³ gives 68.63 as the specific rotation of 10 parts of sugar dissolved in a mixture of 67 parts methyl alcohol and 23 parts water. He also found the specific rotations in ethyl alcohol, and in acetone, mixed with water in the same proportions to be 66.83 and 67.40 respectively. With the exception of these results, there are apparently no data published concerning the optical rotatory power of sugar in solvents other than water.

The effect of various solvents upon the rotation of other optically active substances has been investigated by Freundler,⁴ Landolt, and Pribram; also, recently, by Patterson,⁵ and by Purdie and Barbour.⁶ Various theories have been advanced to explain the variations of the specific rotation with concentration, temperature, and nature of the solvent used. Among these may

¹ Complete references are given in Landolt, "Das optische Drehungsvermögen organischer Substanzen," Zweite Auflage, pp. 171-173, 530, 531.

² Ann. Chim. Phys. (7) 23, 289 (1901).

³ Ber. chem. Ges. Berlin, 13, 2303 (1880).

⁴ References are given in Landolt. l. c. pp. 182, 183.

⁵ Jour. Chem. Soc. 79, 167, 477 (1901).

⁶ Ibid., 79, 971 (1901).

be mentioned the assumption of polymerization of the active molecules in solution, the dissociation theory, chemical action between solvent and dissolved substance, and the recent theory supported by Patterson that variations in specific rotation are dependent upon changes of internal pressure in the solution. It is evident that a vast amount of work must still be done before sufficient data can be accumulated upon which to base satisfactory conclusions in regard to these theories. It is not the intention to discuss the theories here; but the results of the following investigation are submitted in the hope that they may prove useful in the ultimate solution of the apparently complicated problem of the effect of the properties of the solvent on the specific rotation of the dissolved substance.

About three years ago Prof. Kahlenberg found that cane sugar is moderately soluble in pyridine; and recently at his suggestion, I undertook to determine the specific rotatory power of such solutions at various concentrations and at different temperatures. This work seemed of particular interest, because of the great importance of cane sugar in every-day life, and also because of its scientific importance in connection with the development of the present theory of solutions. Again, the fact that pyridine is a solvent in which salts, when dissolved, conduct electricity, gave additional interest to the investigation.

A 6.25 percent solution of sugar in pyridine is nearly saturated, consequently the range of concentrations, the rotations of which can be measured, is small. On the other hand, the high boiling-point of pyridine and the low temperature at which it solidifies, make it possible to obtain results through a relatively great range of temperature. Measurements were made at temperatures varying from -10° to $+105^{\circ}$. Below -10° satisfactory constancy of temperature could not be obtained during the hot summer weather in which the work was carried on. It would, no doubt, be comparatively easy in winter to measure the rotation at -50° or -60° .

The pyridine used was purchased from Kahlbaum. After drying it for several days with fused caustic potash, it was dis-

tilled and the portion passing over between 113.5° and 115° , under 737.8 mm pressure, was used in determining the specific rotation. The density of this fraction was 0.9735 at 25° . The density of the distillate above 115° decreased quite rapidly. The purest loaf sugar obtainable in the market was used in the experiments. It was first pulverized in a mortar and then kept for about half an hour at a temperature of 90° to 100° to expel moisture. Three solutions of 8 g of this sugar in 120 g of water gave 66.8, 66.6, and 66.5 respectively as the values for $[\alpha]_D$ at 25° .

To prepare a solution of 8 g of sugar in 120 g of pyridine, it was necessary to heat the pyridine to the boiling-point in a paraffin bath in order to dissolve all the sugar. Although this made a nearly saturated solution, no sugar crystallized out on cooling, even to temperatures below zero. Four such solutions in which the pyridine was distilled at different times, but under approximately the same conditions, gave 83.9, 83.7, 83.8, and 83.6 respectively, as the specific rotation at 25° . The average of these results is 83.75, a value more than 25 percent greater than that obtained for sugar in aqueous solutions.

To find out whether sugar combines chemically with pyridine to form a crystallizable compound, 40.79 g of a 6.74 percent solution was placed under a bell-jar over concentrated sulphuric acid and left until most of the pyridine had been taken up by the acid. While still slightly moist with pyridine the residue weighed 2.7922 g. The calculated amount of sugar in the solution was 2.7492. Apparently no compound is formed. The sugar did not crystallize out from this solution as the pyridine evaporated, but a thick syrup was formed of about one-sixth the original volume. A fine particle of sugar introduced into this syrup caused some small crystals to form, but most of the sugar was deposited as a hard and apparently amorphous mass, which dissolved rather slowly in water. A second attempt to obtain a supersaturated solution in order to measure its rotation failed, crystals being formed on the dish at the surface of the solution.

The polariscope¹ used was of the Landolt-Lippich type with triple field, made by Schmidt and Haensch. The circular scale was divided into quarter degrees and the verniers permitted readings to be made to hundredths of a degree. The tube containing the solution was made of brass and was 1 dm long. It was mounted in a brass box covered with asbestos, as described by Landolt.² To prevent the deposit of moisture at low temperatures on the glass plates closing the ends of the tube, cylindrical glass caps containing calcium chloride below the line of sight were fitted by ground glass joints over the brass screw caps at the ends of the tube. A little vaseline made the joints moisture proof. Sodium light was obtained by suspending common salt in a platinum basket over a Bunsen burner.

All densities were determined with an Ostwald-Sprengel pycnometer of 10.507 cc capacity. Temperatures were measured with a thermometer graduated to fifths of a degree.

The specific rotation was calculated according to the usual formula, $[\alpha]_D' = \frac{\alpha_D' \times 100}{l \times p \times d}$, in which $[\alpha]_D'$ represents the specific rotation for sodium light at the temperature t ; α_D' , the rotation read on the scale of the polariscope; l , the length of the tube in decimeters; p , the number of grams of sugar in 100 g of solution; and d , the density of the solution.

To determine the effect of concentration upon the specific rotation, four solutions of sugar in pyridine, containing, 1, 2, 4, and 6.25 percent of sugar respectively, were used. The 6.25 percent solution was prepared, as already described, by dissolving 8 g of sugar in 120 g of pyridine. Four g of this solution containing 0.25 g of sugar were then diluted with pyridine until the solution weighed 25 g and, hence, contained 1 percent of sugar. Eight g and 16 g of the 6.25 percent solution were then diluted in the same manner to 25 g to make the 2 percent and 4 percent solutions. The rotation was measured at 25° as soon as the solutions were prepared, and again after two days as a test for birotation. After standing for this length of

¹ This instrument is fully described by Landolt. 1. c. p. 321.

² 1. c. p. 322.

time, none of the solutions gave results which varied more than 0.01° . Each measurement represents the average of five settings of the polariscope.

The following results were obtained :

Percent of sugar	Density of solution	α_D^{25}	$[\alpha]_D^{25}$
1	0.9805	0.62°	86.7
2	0.9829	1.69	85.9
4	0.9912	3.36	84.7
6.25	1.0010	5.23	83.6

The curve obtained by representing percentages of sugar as abscissas and specific rotations as ordinates (Fig. 1) shows the decrease in specific rotation to be almost proportional to the con-

Fig. 1

centration. The slope of the curve is much greater than that of the curve obtained from Tollens' ¹ results for sugar in aqueous solutions of corresponding range in concentration, and it is in the opposite direction.

To calculate the specific rotation of sugar in the pure con-

¹ Landolt. 1. c. p. 173.

dition by the usual method from these results would be useless, since the solubility is too small to give a sufficient range in concentration. It was intended to extend the curve by using super-saturated solutions, but the attempt failed.

Water mixed with the pyridine has a marked effect upon the specific rotation of the dissolved sugar. Two solutions were prepared, one of 8 g of sugar in 120 g of pyridine, the other of 8 g of sugar in 120 g of water. These were mixed in varying proportions, and the rotations of the resulting solutions were measured at 25°. The following table gives the results obtained, and they are also represented graphically in Fig. 2.

Percent of pyridine solution	Percent of water solution	Density	$\alpha_D^{25^\circ}$	$[\alpha]_D^{25^\circ}$
100	0	1.0005	5.24°	83.8
90	10	1.0120	4.93	77.9
80	20	1.0206	4.67	73.2
60	40	1.0263	4.44	69.4
40	60	1.0269	4.31	67.2
20	80	1.0255	4.23	66.0
0	100	1.0224	4.26	66.6

Fig. 2

The mixture containing 10 percent of the pyridine solution shows a slightly lower rotation than a pure aqueous solution ; while 10 percent of the aqueous solution lowers the rotation in pyridine more than 7 percent.

The curve obtained by using the densities of these mixtures as ordinates and the proportion of aqueous solution in the mixture as abscissas, is interesting because it shows a maximum density for a mixture containing about 50 percent of each solution. Pyridine forms a compound with water,¹ the formula of which is $C_5H_5N + 3H_2O$, and, apparently, the form of the curve is due, in part at least, to the presence of this hydrate.

Fig. 3

The effect of temperature was next investigated. For temperatures above 25° the rectangular brass vessel in which the tube of the polariscope was mounted was filled with lard oil after filling the tube with a 6.25 percent solution of sugar in pyridine. The whole was then placed on the open bed of the polariscope and heated with a Bunsen burner to 105° . During the heating the parts of the polariscope were protected as much as possible

¹ Calm Buchka, "Chemie des Pyridins," p. 50.

with screens of asbestos. The temperature was kept constant within a few tenths of a degree for from 20 to 30 minutes by regulating the gas supply and stirring the oil bath. When all distortion of the field, on account of convection currents in the solution and on account of unequal heating of the glass plates closing the ends of the tube, had disappeared, five readings of the polariscope were taken. The average of these readings gave the rotation, when the zero reading, previously determined, was subtracted. The different readings usually did not vary more than two or three hundredths of a degree. The chief sources of error were the difficulty in keeping a constant temperature during the readings, and the absorption of light by the greenish colored compound formed by the slight action of the pyridine on the brass tube, particularly at high temperatures. As far as could be determined, this action did not alter the rotation appreciably, but the absorption of light was at times a serious annoyance, as it increased the difficulty in obtaining accurate readings. A glass tube would have been preferable to a brass one, but it would have been somewhat difficult work to properly mount such a tube in the apparatus for high temperatures.

After the readings at 105° had been taken, the tube with its surrounding jacket, was removed from the bed of the polariscope and allowed to cool to the temperature of the next observation, when it was replaced and readings were again taken in the same manner as before.

The zero of the polariscope was tested between each set of readings, and was found to remain practically unchanged. To determine the zero, readings were taken with the tube filled with distilled water and also with the tube removed. These agreed within the limit of error in reading the polariscope. To see whether heating the glass plates closing the ends of the tube introduced an error in the rotation, the tube was filled with distilled water and the temperature raised to 90° . At first the lines of the field were distorted and blurred, but, after 15 or 20 minutes, the field became clear again and the average of five readings gave the same result as at 25° .

For temperatures below 25° , ice and water, melting ice, or ice and salt were used, as required, in the box surrounding the tube, and the glass caps containing calcium chloride, previously mentioned, were put in place over the ends of the tube to prevent moisture from collecting and interfering with the transmission of light.

At the end of the high temperature series, the rotation at 25° was found to have increased by about one-hundredth of a degree; possibly this was due to evaporation of the pyridine through the small vertical tube into which the solution expanded. Reheating to 105° gave the same result as at first. The results are tabulated on p. 596. They are also given in graphic form in Fig. 4. A repetition of the series with a new solution gave the same values of the rotation within one or two hundredths of a degree.

Fig. 4

Corrections have been applied to these results for the change in length of the brass tube with change of temperature. Assuming that the tube was 1 dcm long at 25° , then,

since the coefficient of linear expansion of brass is 0.000019, its length will be 1.0015 dm at 105°, and 0.9993 dm at -10°. The corrections are small and do not alter the results as given except the last two, which are decreased by one unit in the first decimal place.

6.25 Percent Solution of Sugar in Pyridine

Temperature	Density	α'_D	$[\alpha]_D$
-10°	1.034	5.73°	88.7
0	1.0248	5.59	87.3
+10	1.0150	5.43	85.6
25	1.0005	5.24	83.8
45	0.9811	5.03	82.0
65	0.9619	4.83	80.3
85	0.9420	4.63	78.5
105	0.9220	4.40	77.0

The temperature curve (Fig. 4) indicates that the rate of change in specific rotation is greatest below 25°. This was the most difficult region in which to maintain constant temperatures in warm weather, and the observations, except the one at 0°, are possibly a little less accurate than those above 25°, but the increased steepness of the curve was verified by a number of concordant measurements.

The comparison curve of sugar in water was drawn from the following results of a series of three measurements of a 6.25 percent solution :

Temperature	Density	α'_D	$[\alpha]_D$
0°	1.0254	4.33°	67.60
25	1.0222	4.28	66.99
90	0.9921	4.07	65.59

The specific rotation of this solution at 25° is unusually high. Considering the curve a straight line, which it probably is not, the temperature coefficient would be about 0.0223, a value considerably greater than 0.0144, which was obtained by Schönrock¹ for temperatures from 12° to 25°. The work done on the

¹ Landolt. l. c. p. 531.

temperature coefficient of sugar in water seems to have been confined to a very limited range of temperatures. Pellat¹ came to the conclusion that the rotation changed, if the solution was heated much above 30°. A more extended research in this direction would be of interest.

From a comparison of the two curves in Fig. 4, it is evident that the specific rotation of sugar in pyridine decreases much more rapidly as the temperature increases. The same statement may be made in regard to the density of the two solutions. The density of a 6.25 percent aqueous solution at 0° is 1.0254; at 90° it is 0.9921, a difference of 0.0333. The density of a 6.25 percent pyridine solution is 1.0248 at 0°, and 0.9420 at 85°, a difference of 0.0828. This comparison suggests that the property of pyridine, which causes it to expand more rapidly than water with increase of temperature, also influences the specific rotation of the sugar dissolved in it.

To test further the behavior of sugar in this solvent, its molecular weight was determined by the boiling-point method. A modified form of Beckmann's apparatus was used. Instead of a vapor jacket around the glass tube containing the solvent, an asbestos jacket was used and the whole was placed on a sand-bath. A Beckmann thermometer, graduated to hundredths of a degree was fitted into the tube with a cork. Garnets, to the depth of about 2 cm, and a few pieces of platinum were placed in the bottom of the tube. A condenser was attached to the tube by a side neck and the sugar was introduced through the condenser in the usual way. The pyridine used for this determination distilled over between 114.5° and 115° under 737 mm pressure.

As has been pointed out by Innes,² it is necessary to boil the pyridine several hours in order to obtain a constant boiling-point. In the first series the boiling was continued 10 hours, in the second series 7 hours. The boiling-point constant used in calculating the results was 29.5. This is about the value ob-

¹ I. c.

² Jour. Chem. Soc. 79, 261 (1901).

tained by the Trouton-Schiff rule, $0.00096 \times 388 \times 79 = 29.43$.¹ Werner's² empirical value, 30.07, gives molecular weights about 5 or 6 units higher.

1st Series (9.73 g solvent used)

Sugar	Sugar in 100 g. pyridine	Barometer	Temp. change	Mol. wt.
0.1742 g	1.790 g	737.3	0.163°	324
0.3138	3.225	"	0.275	346
0.5375	5.525	"	0.450	362

2nd Series (14.84 g solvent used)

0.1417 g	0.955 g	739.9	0.110°	256. ³
0.3612	2.434	"	0.235	305.5
0.5582	3.761	"	0.355	312.6
0.7640	5.148	"	0.465	326.6

Mr. Alva Eighmy, in an unpublished thesis, a copy of which is in the library of the University of Wisconsin, gives a series of determinations of the molecular weight of sugar in pyridine. Mr. Eighmy used 16.45 g of pyridine and continued the preliminary boiling about four hours. He computed the molecular weights, using 30.07 as the constant for pyridine, and obtained the following results:

Sugar	Sugar in 100 g. pyridine	Temp. change	Mol. wt.
0.3387 g	2.059 g	0.215°	287.8
0.4927	2.995	0.305	295.0
0.6818	4.145	0.410	303.7
0.8172	4.986	0.475	324.8

In general, the molecular weights are low, and they would still be below the normal, if calculated by Werner's boiling-point constant for pyridine. The only exception is in the first series, where the quantity of solvent was small and the experimental

¹ For a complete discussion of the boiling-point constant, see Innes, l. c., and Kahlenberg, Jour. Phys. Chem. 5, 215 (1901).

² Zeit. anorg. Chem. 15, 1 (1897).

³ Probably an experimental error.

errors relatively large. As sugar is a non-electrolyte when dissolved in pyridine, it should give a normal molecular weight according to the dissociation theory. All the results show a marked increase in molecular weight as the amount of sugar in solution is increased.

In conclusion, I wish to express my thanks to Prof. Kahlenberg, at whose suggestion this work was begun, for the interest he has taken in its progress and for the apparatus and material furnished in his laboratory to carry on the investigation.

Further study of sugar solutions in pyridine is contemplated. A determination of the refractive power and the dielectric constant will soon be made.

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