Rotatory Dispersion of Sugars in Liquid Ammonia and in Water.(1)

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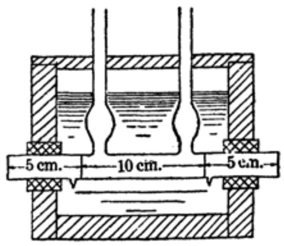
We have attempted to study the nature of sugars in liquid ammonia. In the present paper are reported the results in the preliminary determination of their optical activities at the temperatures below the boiling point of the solvent. The optical rotations of sugars in this medium were measured by Sherry[(2)] at 20°C. for D-line. We were informed by the abstract that Shatenstein recently carried out polarimetric measurements with saponine at 20°C.

To observe the optical rotations at low temperatures, we constructed a polarimetric tube of fused quartz. It has, as shown in Fig. 1, two double windows of plane parallel plates. Both the chambers of the double windows were well evacuated, so that the disturbance by the frost or dew drops condensed on the window plates from the moisture in air was avoided and the field of view was kept clear even when it was cooled down to −70°C. The temperatures, at which we observed, were in the range from −35 to −70°C. and were kept constant within 1° without difficulty during a series of measurements by immersing the tube in a wooden tank of a sufficiently large capacity filled with alcohol and CO_2 snow and covering it externally with felt. We tried to make such a polarimetric tube of borosilicate glass but the glass plates of the windows had fatal strains for our purposes.



The polarimetric tube.

Fig. 1.

The polarimeter used was the three field type of Schmidt and Haensch with a monochromator as its accessory. For the light source the filament lamp 250 W for kinema projection was used through the monochromater which was calibrated with Hg-lines. Mercury, sodium, and cadmium vapour lamps were also used, being filtered with the monochromator. The sugars and the glucoside used were Kahlbaum's or Merck's products.

(1) This paper was read at the autumnal meeting of the Institute of Physical and Chemical Research (Nov. 21, 1935.)

(2) Sherry, *J. Phys. Chem.*, **11** (1907), 559.

For the comparison and the proof of purity of the materials, we determined accurately the rotatory dispersion in water, using the ordinary polarimetric tube 10 cm. long. The results of the measurements were briefly described in the following.

Aqueous Solutions. We determined the rotatory dispersions of *d*-glucose, *d*-fructose, *d*-galactose, *α*-methyl-*d*-glucoside, saccharose, lactose, and maltose in water with high accuracy. In these cases mercury lines ($\lambda = 0.612\,\mu$, 0.578, 0.546, 0.492, 0.436), cadmium lines ($\lambda = 0.644$, 0.509, 0.480), sodium line ($\lambda = 0.589$) were used except saccharose solutions which were observed with the filament lamp. The concentration of solutions is represented in molarities of anhydrous sugars and the specific rotation is evaluated for unit mass of them. Specific rotations obtained were graphed to test Drude's dispersion formula $[\alpha] = k_0/(\lambda^2 - \lambda_0^2)$ and to compare them with the data given by Grossmann and Bloch and by Wagner-Jauregg.(3) Good agreements were obtained as seen in Fig. 2–8. For saccharose such a comparison was omitted and for maltose the previous data of the dispersion to be utilized was not found.

In the cases where the multirotation was to occur, the measurements were carried out 3 or 4 days after preparing the solution. In the duration of preservation, care was taken not to be interfered by fermentation, avoiding the contact of the solutions with air.

Solutions in Liquid Ammonia. The optical rotations in liquid ammonia were measured with the filament lamp as the light source. The measurements were done in the day of preparation of the solution. The accuracy of the rotation measured in liquid ammonia is less than that in water because of using the special polarimetric tube, as mentioned above, at low temperatures. The fluctuation of the experimental values is within $\pm 1\%$ The sugars and glucoside in liquid ammonia were found to behave in the manner of simple rotatory dispersion, although some deviations are seen in the dispersion curve of lactose. The values of λ_0 and k_0 in Drude's formula were estimated from graphs and tabulated in Table 13. As is seen in Table 9, fructose in liquid ammonia showed small rotations with positive or negative sign. It may be roughly assumed that it has not optical activity under our conditions as well as in Sherry's observation at 20°C. Sherry reported that neither in methylamine nor in ethylamine fructose showed measurable optical activity. Such facts seem to suggest something of chemical change of ketose in these mediums.

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(3) "International Critical Tables," Vol. II, 334.

The temperature coefficients of the specific rotation in liquid ammonia were determined for D-line with sodium vapour lamp, as shown in Table 14. We observed also sugars such as glucose, fructose, saccharose, and lactose dissolved in the mixture of water and ethyl alcohol in equal volumes at the room temperature and at low temperatures. The results are shown in Table 15.

Table 1. *d*-Glucose in water.

$^2/_3$ mol, 20–21°C., 3 days after dissolution, Hg-lamp.

λ (μ)	[α]
0.578	53.1
0.546	66.5
0.492	73.9
0.436	120.0

$\lambda_0 = 0.148$ $k_0 = 17.2$

Table 2. *d*-Fructose in water.

$^2/_3$ mol, 20-21°C., the day of dissolution, Hg-, Na-, Cd-lamps.

λ (μ)	[α]
0.644	—
0.612	−83.5
0.589	−93.0
0.578	−98.5
0.546	−110.0
0.509	−127.6
0.492	−128.7
0.480	−145.6
0.436	−181.0

$\lambda_0 = 0.152$ $k_0 = 29.8$

Table 3. *d*-Galactose in water.

$^1/_2$ mol, 21°C., 4 days after dissolution, Hg-, Na-, Cd-lamps.

λ (μ)	[α]
0.644	67.2
0.612	70.6
0.589	79.9
0.578	83.6
0 546	95.2
0.509	112.3
0.492	119.7
0.480	125.2
0.436	154.3

$\lambda_0 = 0.145$ $k_0 = 26.0$

Table 4. *α*-Methyl-*d*-glucoside in water.

$^2/_3$ mol, 20°C., 4 days after dissolution, Hg-, Na-, Cd-lamps.

λ (μ)	[α]
0.644	128.7
0.612	142.6
0.589	158.2
0.578	165.1
0.546	186.0
0.509	218.8
0.492	231.7
0.480	246.7
0.436	308.7

$\lambda_0 = 0.138$ $k_0 = 52.0$

Table 5. Saccharose in water.

0.292 mol, 28.3°C., filament lamp.

λ (μ)	[α]
0.623	57.3
0.589	64.7
0.578	66.4
0.546	76.1
0.517	86.7
0.492	96.4
0.458	105.5
0.436	115.9

1.168 mol, 28°C.

λ (μ)	[α]
0.623	57.8
0.610	60.4
0.600	62.5
0.589	64.8
0.578	67.7
0.565	71.0
0.546	76.6
0.530	81.8
0.510	89.2
0.492	95.7
0.470	105.2
0.450	116.4
0.436	125.0

$\lambda_0 = 0.141$ $k_0 = 21.2$

Table 6. Lactose in water.

$^1/_3$ mol, 19°C., 3 days after dissolution, Hg-, Na-, Cd-lamps.

λ (μ)	[α]
0.644	42.4
0.612	46.1
0.589	52.2
0.578	53.8
0.546	60.3
0.509	71.6
0.492	73.6
0.480	78.9
0.436	98 3

$\lambda_0 = 0.145$ $k_0 = 16.6$

Table 7. Maltose in water.

$^1/_2$ mol, 16°C., 4 days after dissolution, Hg-, Na-, Cd-lamps.

λ (μ)	[α]
0.644	113.9
0.612	124.6
0.589	138.7
0.578	144.7
0.546	164.4
0.509	191.8
0.492	205.0
0.480	216.5
0.436	271.0

$\lambda_0 = 0.173$ $k_0 = 43.6$

Table 8.
d-Glucose in liquid ammonia.

0.48 mol, −35°C., filament lamp.

λ (μ)	[α]
0.644	62.7
0.612	62.7
0.589	77.3
0.578	74.8
0.546	86.0
0.509	108.0
0.492	114.5
0.480	135.7
0.436	153.0

$\lambda_0 = 0.258$ $k_0 = 20.6$

Table 9.
d-Fructose in liquid ammonia.

0.46 mol, −36°C., filament lamp.

λ (μ)	[α]
0.612	+0.09
0.578	−4.18
0.546	−6.11
0.492	+5.47
0.436	−4.39

Table 10. α-Methyl-*d*-glucoside in liquid ammonia.

0.34 mol, −36°C., filament lamp.

λ (μ)	[α]
0.644	140.4
0.612	152.4
0.589	168.2
0.578	180.9
0.546	203.4
0.509	238.5
0.492	259.8
0.480	272.4
0.436	325.1

$\lambda_0 = 0.152$ $k_0 = 55.2$

Table 11.

Saccharose in liquid ammonia.

0.21 mol, −43°C., filament lamp.

λ (μ)	[α]
0.644	63.0
0.612	65.5
0.589	84.6
0.578	83.9
0.546	101.4
0.509	117.3
0.492	125.0
0.480	129.0
0.436	171.0

$\lambda_0 = 0.247$ $k_0 = 22.0$

Table 12.

Lactose in liquid ammonia.

0.19 mol, −51°C, filament lamp.

λ (μ)	[α]
0.644	40.4
0.612	59.0
0.589	62.1
0·578	71.0
0.546	83.4
0.509	96.3
0.492	104.5
0.480	107.0
0.436	122.7

$\lambda_0 = 0.214$ $k_0 = 19.6$

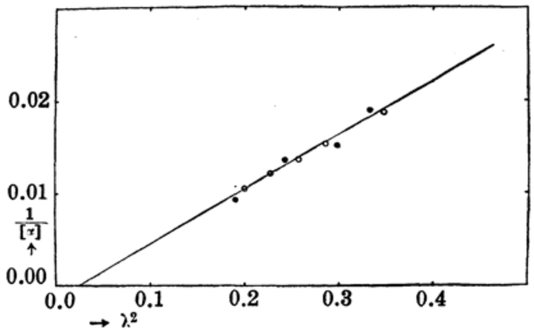

Fig. 2. *d*-Glucose in water. 20–21°C. ○ Grossmann and Bloch.

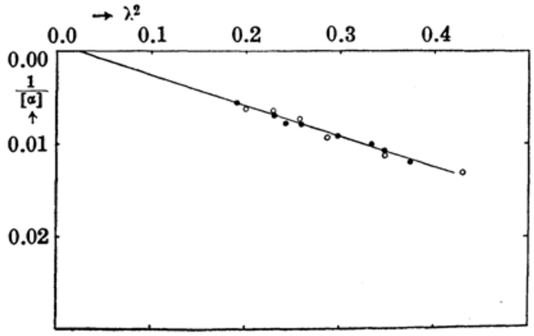

Fig. 3. *d*-Fructose in water. 20–21°C. ○ Grossmann and Bloch.

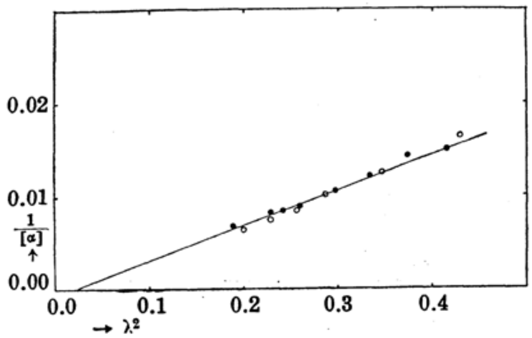

Fig. 4. *d*-Galactose in water. 21°C. ○ Grossmann and Bloch.

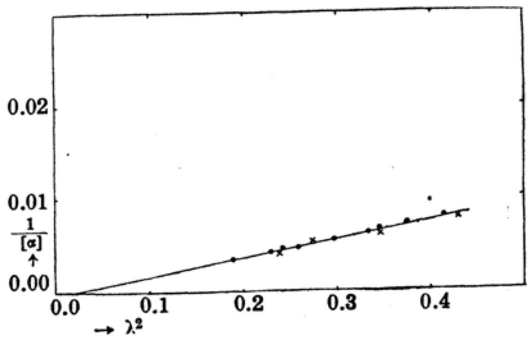

Fig. 5. α-Methyl-*d*-glucoside in water. 20°C. × Wagner-Jauregg.

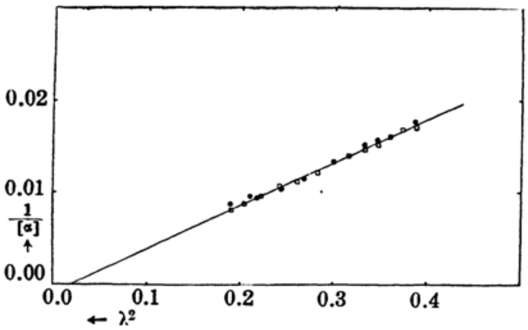

Fig. 6. Saccharose in water.
● 0.292 mol, 28.3°C. □ 1.168 mol, 28.0°C.

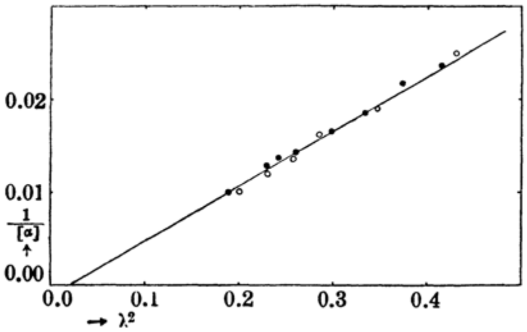

Fig. 7. Lactose in water. 19°C. ○ Grossmann and Bloch.

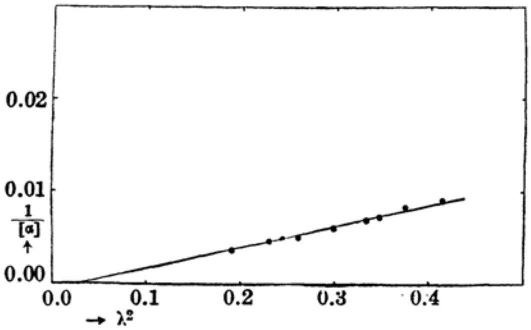

Fig. 8. Moltose in water. 16°C.

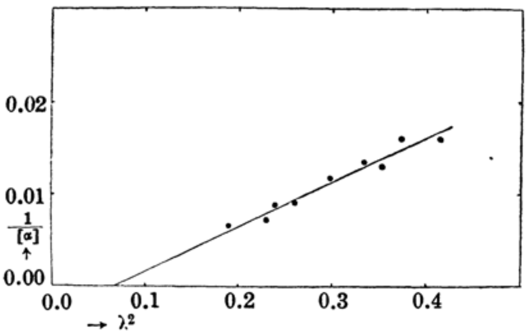

Fig. 9. d-Glucose in liquid NH_3, 0.48 mol, −35°C., filament lamp.

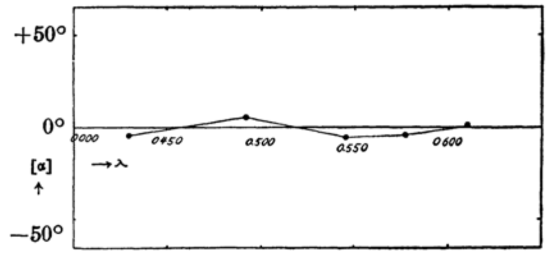

Fig. 10. d-Fructose in liquid NH_3, 0.46 mol, −36°C., filament lamp.

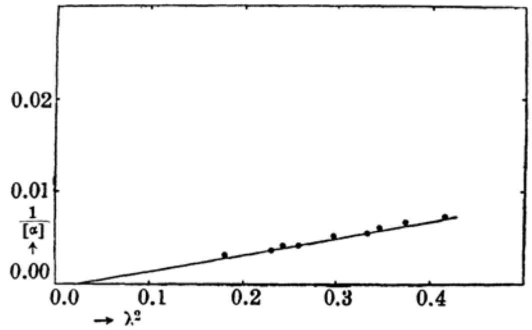

Fig. 11. α-Methyl-d-glucoside in liquid NH_3, 0.34 mol, - 36°C., filament lamp.

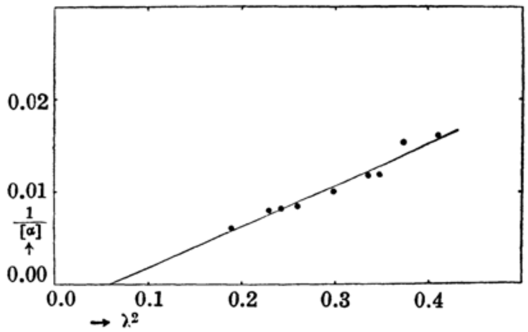

Fig. 12. Saccharose in liquid NH_3, 0.21 mol, −43°C., filament lamp.

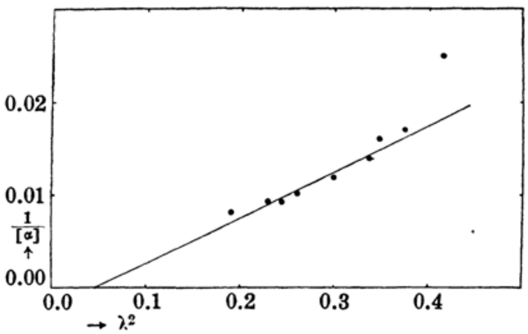

Fig. 13. Lactose in liquid NH_3, 0.19 mol, −51°C., filament lamp.

Table 13. Values of λ_0 and k_0 ($[\alpha] = k_0/(\lambda^2-\lambda_0^2)$).

	Aqueous solution			Solution in liquid NH_3		
	t °C.	λ_0 (μ)	k_0	t °C.	λ_0 (μ)	k_0
d-Glucose	21	0.148	17.2	−35	0.258	20.6
d-Fructose	20–21	0.152	29.8	−36	—	—
d-Galactose	21	0.145	26.0	—	—	—
α-Methyl-*d*-glucoside	20	0.138	52.0	−36	0.152	55.2
Saccharose	28	0.141	21.2	−43	0.247	22.0
Lactose	19	0.145	16.6	−51	0.214	19.6
Maltose	16	0.173	43.6	—	—	—

Table 14. Temperature coefficient of $[\alpha]_D$ in liquid ammonia.

	Concentration	t °C.	$[\alpha]_D$	$\frac{\Delta[\alpha]_D}{\Delta t}$
d-Glucose	0.48 mol	−35	77.3	−0.26
	0.48 mol	−62	84.2	
	3.5 g. in 100 c.c. solution	20	56.1	} Sherry
	27.8 g. in 100 c.c. solution	20	55.3	
d-Fructose	0.46 mol	−36	[0]	
	—	20	0	Sherry
α-Methyl-*d*-glucoside	0.34 mol	−36	168.2	−0.31
	0.34 mol	−54	173.6	
Saccharose	0.21 mol	−43	84.6	−0.20
	0.21 mol	−63	88.6	
	8.2 g. in 100 c.c solution	20	76.0	} Sherry
	48.8 g. in 100 c.c solution	20	73.6	
Lactose	0.19 mol	−42	60.5	−0.18
	0.19 mol	−51	62.1	
	7.0 g. in 100 c.c. solution	20	33.2	} Sherry
	27.8 g. in 100 c.c solution	20	32.5	

Table 15. Temperature coefficient of $[\alpha]_D$ in the mixture of water and ethyl alcohol (equal volumes).

	Concentration	t °C.	$[\alpha]_D$	$\frac{\Delta[\alpha]}{\Delta t}$
d-Glucose	0.5 g. in 100 c.c. solution	23 - 67	59.6 71.6	−0.13
d-Fructose	1 g. in 100 c.c. solution	23 −67.5	−64.8 −76.5	0.13
Saccharose	5 g. in 100 c.c. solution	20 −45	66.5 80.0	−0.20
Lactose	0.2 g. in 100 c.c. solution	23 −67.5	49.1 93.7	−0.53

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