[CONTRIBUTION FROM TOKYO COLLEGE OF SCIENCE]

The Specific Rotation of Fructose at Higher Concentrations

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The specific rotation of fructose has been measured accurately and systematically at temperatures from 10 to 90°, and for concentrations from 50 to 80%. The specific rotation can be expressed by equation (1). An empirical formula in term of c has also been proposed.

In a previous paper[2] we have reported the result of exact measurement of the specific rotation of fructose at lower concentration. This paper aims at presenting a whole series of precise data of the specific rotation and the density of fructose solutions measured systematically with very pure materials at higher concentrations, namely, from 50 to 80% in a wide range of temperature. It is also of no small interest to us to see whether the simple relation of the specific rotation to temperature and concentration still holds at higher concentrations, for the values of the highest concentration reported in the literature (c 48.8)[3] shows some irregularity with respect to temperature.

Experimental

The materials and the method of measurement used in this work are almost the same as described in the previous paper.

We have used three different samples of fructose carefully purified by recrystallizing from water or from dilute alcohol. They melted at 104° and contained about 0.005% of ash. No significant difference was observed with respect to specific rotation, as seen in Table I.

TABLE I

PURIFICATION OF FRUCTOSE

Fructose prepn.	Recrystallized from	$[\alpha]^{20}_D$ (p 50)	$[\alpha]^{30}_D$ (p 60)
1	Water, 2 times	...	−93.80
2	Water, 2 times	−98.57	...
3	Water and then from 75% alcohol	−98.66	−93.79

Results of Measurements.—The results of measurement of the specific rotation of fructose were listed in Table III, where p gives percentage by weight (g. of fructose in 100 g. solution). A greater part of the values are the mean of several observations of different preparations, but the values of 50% above 50° and those of 70% were obtained with a single preparation of fructose (No. 3). Some examples are given in Table II to show the precision of the measurements.

TABLE II

SOME EXAMPLES OF DATA OF MEASUREMENTS

Fructose prepn.	p	d_4	α_D	$[\alpha]_D$
	(1) Temperature, 15.0°			
2	50.010	1.2328	−125.27	−101.59
3	50.014	1.2328	− 62.60	−101.54
	(2) Temperature, 50.0°			
1	59.990	1.2642	− 62.00	− 81.74
3	60.053	1.2651	− 62.07	− 81.69
	(3) Temperature, 80.0°			
1	80.010	1.3579	− 72.83	− 66.92
3	80.021	1.3589	− 72.98	− 67.11

TABLE III

SPECIFIC ROTATION OF FRUCTOSE

t, °C. ↓ / p(%) →	50	60	70	80
10	−104.46	−105.78		
15	−101.57	−102.84		
20	− 98.61	− 99.91	−101.33	−102.68
25	− 95.55	− 96.91	− 98.20	− 99.74
30	− 92.38	− 93.80	− 95.26	− 96.80
40	− 86.33	− 87.78	− 89.32	− 90.96
50	− 80.19	− 81.71	− 83.14	− 84.87
60	− 74.10	− 75.59	− 77.18	− 78.79
70	− 68.21	− 69.62	− 71.19	− 72.84
80	− 62.32	− 63.65	− 65.26	− 67.02
90	− 56.82	− 58.17	− 59.73	− 61.47

In order to get a view on the general trend how the values of the specific rotation of fructose vary with temperature and concentration, the values in Table III are shown in Fig. 1, where the values of

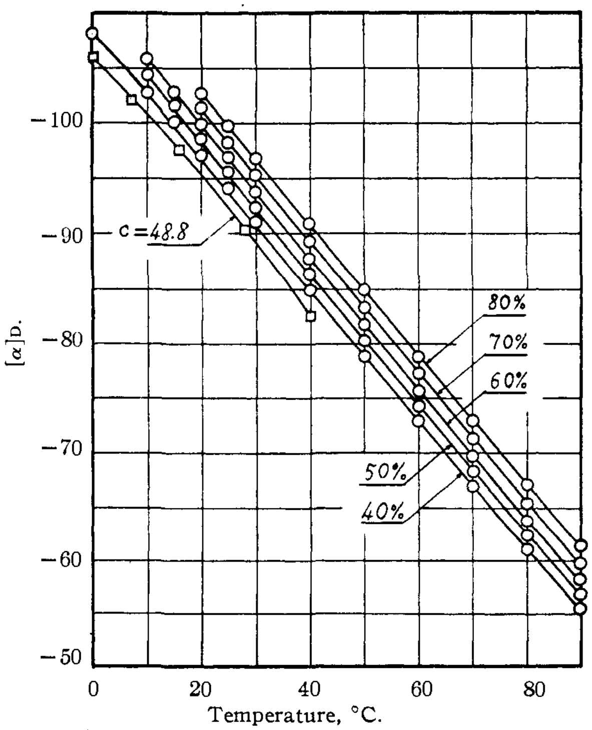

Fig. 1.—Relation between specific rotation and temperature: □, data given by Jungfleisch and Grimbert.[3]

(1) Japan Levulose Co., Kawasaki, Japan.

(2) Y. Tsuzuki, J. Yamazaki and K. Kagami, THIS JOURNAL, **72**, 1071 (1950).

(3) Jungfleisch and Grimbert, *Compt. rend.*, **107**, 392 (1888); Beilstein, "Handbuch der org. Chemie." IV Edition, "Kohlenhydrate," Vol. 31, 1938, p. 324.

Jungfleisch and Grimbert[3] and those at 40% already reported by us are also cited for the sake of comparison.

It may be seen in Fig. 1 that the relation between the specific rotation and temperature is almost linear in the whole range of temperature in contrast with the case of $c = 48.8\%$, and that these straight lines run nearly parallel, as in the case of the lower concentrations, but with a distance increasing regularly with growing concentration.

The values for densities of aqueous solutions of fructose are collected in Table IV.

TABLE IV

DENSITIES OF AQUEOUS SOLUTIONS OF FRUCTOSE

t, °C. → p	50	60	70	80
10	1.2357	1.2927		
15	1.2328	1.2896		
20	1.2301	1.2860	1.3452	1.4068
25	1.2269	1.2823	1.3424	1.4025
30	1.2242	1.2792	1.3378	1.3990
40	1.2176	1.2721	1.3303	1.3915
50	1.2106	1.2647	1.3227	1.3832
60	1.2036	1.2574	1.3145	1.3744
70	1.1962	1.2498	1.3062	1.3661
80	1.1890	1.2415	1.2979	1.3584
90	1.1824	1.2343	1.2906	1.3502

By using the data given in Tables III and IV we are able to express the specific rotations in terms of volume percentage, c, and since their variations with temperature and concentration are quite regular, it is possible, by interpolation, to calculate the values of the specific rotation in a wide range of concentration and temperature with an error usually less than 0.05°. Thus we can compare our results of measurements with those of the previous observers, which were often given in term of percentage by volume. In Table V are shown a few results of our calculations comparing with the data of the highest concentration ever recorded. It is seen from this Table that our values are much higher than those of Jungfleisch and Grimbert.

TABLE V

t, °C.	Jungfleisch and Grimbert[3] $[\alpha]_D$ (c 48.8)	Present authors $[\alpha]_D$ (c 48.8)
16	−97.6	−99.66
28	−90.4	−92.45
40	−82.5	−85.16

Empirical Formulas.—The specific rotation of fructose at higher concentrations can be expressed by means of the equation

$$[\alpha]^t_D = -(103.45 + 0.141p) + (0.584 + 0.0_377p - 0.0_576p^2)t \quad (1)$$

where p is concentration by weight percentage. This equation is based on our experimental results for $p = 50$ to 80% and $t = 10$ to 80°, but also expresses fairly well the values for lower concentrations, namely, from 10 to 40% already reported in the previous paper.[2]

The difference between the calculated and the found in the values of $[\alpha]_D$ lies in most cases under 0.15°.

The specific rotation of fructose can also be expressed by the equation

$$[\alpha]^t_D = -104.35 - 0.094c + 0.596t \quad (2)$$

where c is concentration by volume percentage (g. of fructose in 100 cc. of solution). This equation covers a wider range of concentration than the above, namely, from 20 to 110%, but the difference between the calculated and the found is in some cases larger than that of the equation (1), although in both cases it is smaller than the experimental error.

As seen from the above statement these equations as well as the data obtained for the specific rotation of fructose together with those reported in the previous paper may be available for estimating its concentration with sufficient accuracy by measuring polarimetrically at any temperature and concentration.

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