[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEW YORK STATE AGRICULTURAL EXPERIMENT STATION]

The Solubility of Potassium Acid Tartrate. II.[1] In Various Sugar Solutions

BY D. C. CARPENTER AND J. J. KUCERA

In a previous paper[2] from this Laboratory the solubility of potassium acid tartrate in tartaric acid and di-potassium tartrate solutions was reported. The present work is a continuation of the former, in which the solubility of the acid tartrate in solutions of *d*-glucose, *d*-fructose, invert sugar and sucrose, respectively, has been investigated.

The writers have been unable to find in the literature any reference to the solubility of potassium acid tartrate in sugar solutions. As to other salts, Weber[3] reports that sucrose and mannitol have very little effect on the solubility of di-potassium sulfate.

Experimental Part

Preparation of Materials.—Potassium acid tartrate was prepared from C. P. potassium hydroxide and tartaric acid as previously described. The purity of the salt was ascertained by a potassium analysis.

Anal. Calcd. for ($KHC_4H_4O_6$): K, 20.78. Found: K, 20.77, 20.78, 20.76, av. 20.77.

d-Fructose was recrystallized twice by the method described by Jackson and Mathews,[4] then washed with absolute alcohol, sucked dry on a Buchner funnel and finally dried in a vacuum oven at 50° and kept in a vacuum desiccator over phosphorus pentoxide at room temperature. Purity of the crystalline *d*-fructose was ascertained by the following optical rotation, melting point and ash determinations; $[\alpha]^{20}_{D}$ −95.25°, m. p. 109–110° and ash 0.05%. The *d*-glucose and sucrose used were C. P. preparations which were not further purified except to filter the stock solutions used in making up the various concentrations required in the solubility experiments. The purity of these sugars was judged by the same criteria as above: for *d*-glucose, $[\alpha]^{20}_{D}$ 52.41°, m. p. 160° and ash 0.02%; for sucrose $[\alpha]^{20}_{D}$ 66.50°, m. p. 189°, and ash 0.03%.

For our experiments we have prepared invert sugar from the pure sugars *d*-glucose and *d*-fructose described above by adding weighed amounts of each sugar in equal proportions.

Experimental Method

Concentrated stock solutions of the various sugars were prepared from the pure compounds, for use in preparing the various concentrations of each required in the solubility determinations reported below. Appropriate quantities of the stock solutions were added as required to an excess of potassium acid tartrate in a clean dry 125-ml. Erlenmeyer flask and the mixture made up to 100 g. of the final concentration with distilled water which had been recently boiled to remove carbon dioxide.

In order to approach the equilibrium for potassium acid tartrate from both the under and supersaturated sides, half of the solutions prepared as above were supersaturated with respect to potassium acid tartrate by immersing the flasks in warm water and shaking until more of the salt dissolved than was required for saturation at the respective temperatures. The flasks were kept tightly stoppered to prevent escape of water vapor during the warming operation, and to prevent inward diffusion of water after submersion in the constant temperature bath.

The flasks containing the solutions were placed in a McMeekin–Koch shaking machine immersed in a water thermostat controlled to within ±0.05° and agitated continuously until equilibrium was reached, at the end of which time the solutions for analysis were removed by suction through a capillary tube as described before.

Potassium was determined on the weighed sample of solution by the perchlorate method, after oxidizing the sugar and tartrate radical with nitric acid. This procedure takes some time and care but requires little attention after the bulk of the organic matter is oxidized. Potassium is thereby obtained as the nitrate and can be treated with perchloric acid as usual. Anhydrous ethyl alcohol containing 0.2% $HClO_4$ was used as wash liquid. Correction for the small amount of potassium perchlorate dissolved in the wash liquid was made as described in the previous paper.

On account of the high viscosity of the more concentrated sugar solutions, the time required for the establishment of equilibrium was considerably greater than has been noted in the former paper of this series. To be certain of having reached equilibrium conditions, we have continued shaking at constant temperature for the time interval of five days at 20°, seven days at 15°, ten days at 10°, fifteen days at 5° and twenty-one days at 0°.

All solutions and determinations were made by weight and the weights used were compared directly with a set calibrated by the U. S. Bureau of Standards. The density of a large number of the solutions was determined in a carefully calibrated pycnometer of about 50-ml. capacity.

---

[1] Approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 6.

[2] Carpenter and Mack, THIS JOURNAL, **56**, 311 (1934).

[3] Weber, *Z. anorg. allgem. Chem.*, **181**, 385–394 (1929).

[4] Jackson and Mathews, *Bur. Standards J. Research*, **8**, 403–444 (1932).

TABLE I

SOLUBILITY OF POTASSIUM ACID TARTRATE IN *d*-GLUCOSE SOLUTIONS

	0°		5°		10°		15°		20°	
Wt. % *d*-glucose	KHT per 100 g. soln., g.	Density 0°/4°	KHT per 100 g. soln., g.	Density 5°/4°	KHT per 100 g. soln., g.	Density 10°/4°	KHT per 100 g. soln., g.	Density 15°/4°	KHT per 100 g. soln., g.	Density 20°/4°
0	0.2305	1.0012	0.2870	1.0016	0.3579	1.0020	0.4338	1.0016	0.5323	1.0012
10	.2251	1.0406	.2766	1.0411	.3356	1.0412	.4091	1.0411	.4924	1.0405
20	.2114	1.0828	.2576	1.0833	.3161	1.0834	.3812	1.0832	.4442	1.0824
30	.1982	1.1278	.2381	1.1283	.2910	1.1283	.3458	1.1281	.4010	1.1272
40	.1778	1.1789	.2188	1.1793	.2633	1.1793	.3070	1.1791	....	1.1781

TABLE II

SOLUBILITY OF POTASSIUM ACID TARTRATE IN *d*-FRUCTOSE SOLUTIONS

	0°		5°		10°		15°		20°	
Wt. % *d*-fructose	KHT per 100 g. soln., g.	Density 0°/4°	KHT per 100 g. soln., g.	Density 5°/4°	KHT per 100 g. soln., g.	Density 10°/4°	KHT per 100 g. soln., g.	Density 15°/4°	KHT per 100 g. soln., g.	Density 20°/4°
1	0.2298	1.0052	....	....	0.3553	1.0059	0.4359	1.0058	0.5301	1.0052
5	.2264	1.0210	0.2830	1.0216	.3534	1.0197	.4315	1.0217	.5180	1.0210
10	.2241	1.0415	.2803	1.0420	.3446	1.0421	.4163	1.0421	.5037	1.0414
20	.2182	1.0846	.2644	1.0851	.3234	1.0852	.3883	1.0851	.4637	1.0843
30	.2072	1.1307	.2533	1.1311	.3039	1.1312	.3660	1.1312	.4269	1.1303
40	.1943	1.1803	.2328	1.1807	....	....	....	....	.3833	1.1796

TABLE III

SOLUBILITY OF POTASSIUM ACID TARTRATE IN INVERT SUGAR SOLUTIONS

	0°		5°		10°		15°		20°	
Wt. % invert sugar	KHT per 100 g. soln., g.	Density 0°/4°	KHT per 100 g. soln., g.	Density 5°/4°	KHT per 100 g. soln., g.	Density 10°/4°	KHT per 100 g. soln., g.	Density 15°/4°	KHT per 100 g. soln.,	Density 20°/4°
1	0.2295	....	0.2818	....	0.3544	....	0.4316	....	0.5290	....
5	.2282	1.0209	.2812	1.0214	.3500	1.0216	.4273	1.0215	.5171	1.0209
10	.2246	1.0412	.2786	1.0417	.3394	1.0418	.4164	1.0417	.4979	1.0411
20	.2144	1.0840	.2613	1.0845	.3202	1.0846	.3848	1.0845	.4570	1.0837
30	.2010	1.1300	.2395	1.1305	.2918	1.1305	.3510	1.1304	.4152	1.1296
40	.1828	1.1794	.2224	1.1799	....	....	....	....	.3700	1.1788

TABLE IV

SOLUBILITY OF POTASSIUM ACID TARTRATE IN SUCROSE SOLUTIONS

	0°		5°		10°		15°		20°	
Wt. % sucrose	KHT per 100 g. soln., g.	Density 0°/4°	KHT per 100 g. soln., g.	Density 5°/4°	KHT per 100 g. soln., g.	Density 10°/4°	KHT per 100 g. soln., g.	Density 15°/4°	KHT per 100 g. soln., g.	Density 20°/4°
10	0.2241	1.0410	0.2681	1.0414	0.3228	1.0415	0.3933	1.0414	0.4715	1.0409
20	.1955	1.0839	.2394	1.0844	.2924	1.0843	.3530	1.0843	.4237	1.0835
30	.1723	1.1299	.2098	1.1303	.2532	1.1302	.3028	1.1301	.3707	1.1293
40	.1503	1.1792	.1797	1.1796	.2180	1.1795	.2561	1.1793	.3114	1.1784
50	.1257	1.2322	.1490	1.2326	.1752	1.2325	.2145	1.2322	.2568	1.2313

Results and Conclusions

In Tables I, II, III and IV are recorded the solubility of potassium acid tartrate in various concentrations of *d*-glucose, *d*-fructose, invert sugar and sucrose solutions, respectively, at 0, 5, 10, 15 and 20°. The recorded values in each case represent means of several determinations in which the equilibrium at each temperature was approached from both directions.[5] The data are shown graphically in Figs. 1 and 2.

It has been found that the solubility of potassium acid tartrate in the various sugar solutions at various temperatures may be expressed by the general equation $C_{\text{KHT}} = K - kC^{a}_{\text{Sugar}}$ in which C_{KHT} and C_{Sugar} represent the concentration in milligrams per 100 g. of solution, respectively, of potassium acid tartrate and of the sugar under consideration, K represents the solubility of the acid tartrate in water and k and a are constants depending on temperature and kind of sugar. In Table V are given solubility values calculated by the above formulation for the temperatures 0, 10 and 20°. In this table the constants given are

---

(5) The writers are indebted to Dr. G. L. Mack for certain values on the solubility of potassium acid tartrate in water, which results have been averaged with our own in arriving at the average values given in Table I.

TABLE V

SOLUBILITY OF POTASSIUM ACID TARTRATE IN SUGAR SOLUTIONS CALCULATED FROM $C_{KHT} = K - kC^{a}_{sugar}$

	Temperature, 0°C.	Temperature, 10°C.	Temperature, 20°C.
	$K = 230.5$	$K = 358$	$K = 532$
	$k_g = 0.0000263$; $a_g = 1.546$	$k_g = 0.09940$; $a_g = 1.080$	$k_g = 0.05224$; $a_g = 1.082$
	$k_f = 0.0005663$; $a_f = 1.366$	$k_f = 0.00597$; $a_f = 1.235$	$k_f = 0.00379$; $a_f = 1.250$
	$k_i = 0.0000178$; $a_i = 1.505$	$k_i = 0.00132$; $a_i = 1.100$	$k_i = 0.08586$; $a_i = 1.117$
	$k_s = 0.00315$; $a_s = 1.179$	$k_s = 0.03983$; $a_s = 1.030$	$k_s = 0.01826$; $a_s = 1.000$

Concn., %	Concn. KHT mg. per 100 g. soln.		Concn. KHT mg. per 100 g. soln.		Concn. KHT mg. per 100 g. soln.	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
d-Glucose						
10	225	225	336	337	492	491
20	211	214	316	313	444	446
30	198	199	291	290	401	398
40	178	181	263	265	349	350
d-Fructose						
5	226	229	353	352	518	521
10	224	225	345	343	504	506
20	218	217	323	324	464	469
30	207	208	304	301	427	428
40	194	196	...	...	383	383
Invert sugar						
5	228	228	350	349	517	516
10	225	225	339	339	498	498
20	214	214	320	317	457	458
30	201	200	292	294	415	416
40	183	183	...	...	370	371
Sucrose						
10	224	216	323	325	472	477
20	196	195	292	290	424	423
30	172	174	253	253	371	368
40	150	150	218	220	311	313
50	126	126	175	184	257	258

expressed on the basis of milligrams per 100 g. of solution. Considering the small number of experimental points available for calculation of the constants, it is seen that the calculated values agree fairly well with the experimental values over the concentration range studied.

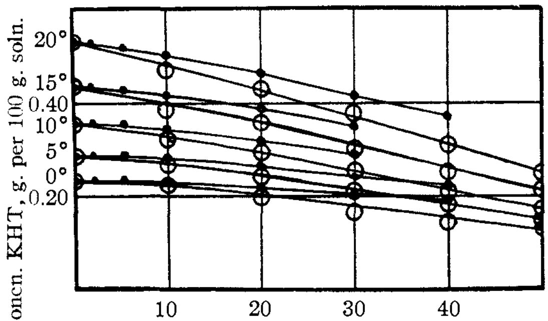

Fig. 1.—Solubility of potassium acid tartrate in sucrose and invert sugar solutions at various temperatures: ⊙, sucrose; ●, invert sugar.

Inasmuch as sucrose would be inverted very slowly in the presence of potassium acid tartrate, we have measured the extent of the inversion in 20 and 50% sucrose solutions at 20° saturated with respect to potassium acid tartrate. Our results show that after five days 0.33% of the sucrose present was inverted in a 20% solution and 0.27% in a 50% sucrose solution. Greater inversion in

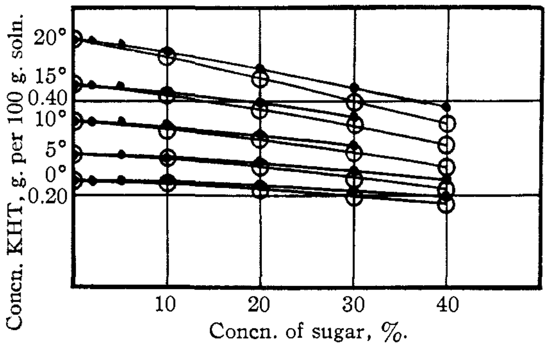

Fig. 2.—Solubility of potassium acid tartrate in *d*-glucose and *d*-fructose solutions at various temperatures: ⊙, *d*-glucose; ●, *d*-fructose.

the more dilute sucrose solution is probably due largely to the greater amount of potassium acid tartrate soluble in a 20% solution as compared with a 50% sucrose solution. These results, while they indicate that a slow inversion of sucrose no doubt takes place which would be completed over a long time period and affect the solubility data, show that the correction is of too small magnitude to be considered as a factor in attaining solubility equilibrium in our work.

From the data it appears that the solubility of potassium acid tartrate decreases in the presence of sugars as the concentration of the latter is increased. Arranged in their order of increasing effectiveness in reducing the solubility of the acid tartrate, the sugars take the order *d*-fructose, invert sugar, *d*-glucose and sucrose.

It was of interest to calculate the solubility of potassium acid tartrate in the various sugar solutions to a common basis such as the water basis, to note any solubility effect due to the nature of the sugar. It was found that *d*-fructose, invert sugar and *d*-glucose increased the solubility of acid tartrate (on a fixed water basis) as the sugar content was increased, the first mentioned having the greater effect. On the other hand, the sucrose concentration had little effect on the amount of acid tartrate dissolved in a fixed weight of water. We are inclined to attribute this effect to the presence of the highly reactive ketone group in *d*-fructose, while the aldehyde group in *d*-glucose is presumably less reactive, and the respective groups in sucrose are inactive due to internal linking within the disaccharide molecule.

Summary

1. The solubility of potassium acid tartrate in solutions of *d*-glucose, *d*-fructose, invert sugar and sucrose has been determined for a series of sugar concentrations at 0, 5, 10, 15 and 20°.

2. The solubility of the acid tartrate in the various sugar solutions at various concentrations may be expressed by the general equation $C_{\text{KHT}} = K - kC^{a}_{\text{Sugar}}$, in which C_{KHT} and C_{Sugar} represent the concentration in milligrams per 100 g. of solution, respectively, of potassium acid tartrate and of the sugar under consideration. K represents the solubility of the acid tartrate in water and k and a are constants which depend on the temperature and the kind of sugar.

3. The solubility of potassium acid tartrate decreases in the presence of sugars as the concentration of the latter is increased. Arranged in their order of increasing effectiveness in reducing the solubility of the acid tartrate, the sugars take the order, *d*-fructose, invert sugar, *d*-glucose and sucrose.

4. When calculated on the basis of a fixed amount of water as solvent, it has been found that the solubility of potassium acid tartrate is noticeably increased by increasing concentrations of *d*-fructose, invert sugar and *d*-glucose but is practically unchanged by increasing concentrations of sucrose.

GENEVA, N. Y. RECEIVED SEPTEMBER 15, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Role of Oxygen as an Inhibitor for the Photosynthesis of Hydrogen Chloride

BY K. B. KRAUSKOPF AND G. K. ROLLEFSON

When a mixture of H_2, O_2 and Cl_2 is illuminated with light absorbed by Cl_2, part of the H_2 combines with Cl_2 and part with O_2. The relative amounts of HCl and H_2O formed depend on the O_2/Cl_2 ratio. An investigation of the amounts formed when this ratio is large affords a direct means of determining whether the well-known inhibiting effect of O_2 on the HCl reaction is due to a reaction with H atoms or to a reaction with Cl atoms.

Thus, suppose that the initial pressure of O_2 is increased rapidly in successive runs. If a reaction between O_2 and Cl occurs to any great extent, the amount of HCl formed should fall off regularly until finally the Nernst chains fail to start at all. On the other hand, if a reaction between O_2 and H predominates, HCl production can never fall to zero, but should approach some small limiting value, since the formation of an H atom requires the simultaneous production of an HCl molecule. Water formation in the first case should eventually become much larger than HCl formation, but in either case should remain small.