should be attached to this figure. It is hoped, however, that the preparation of radiographs may assist in indicating the less altered portions of the material and, if so, an age determination of the unaltered portion may have greater significance.

Summary

A study of the J. Lawrence Smith method of analyzing samarskite has been made, showing how the different elements distribute themselves in the treatment with hydrofluoric acid. Precautions to be observed in completing the different determinations are given.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PITTSBURGH]

THE HYDROLYSIS OF SUCROSE BY HYDROCHLORIC ACID IN THE PRESENCE OF ALKALI AND ALKALINE EARTH CHLORIDES[1]

BY C. F. KAUTZ AND A. L. ROBINSON

RECEIVED DECEMBER 7, 1927 PUBLISHED APRIL 5, 1928

The Influence of Neutral Salts on the Acid Inversion of Sucrose

Introduction

It has long been known that neutral salts exert an accelerating influence on reactions of substances subject to catalytic decomposition in acid solutions. Since the original discovery of this phenomenon in the case of sugar hydrolysis by Löwenthal and Lenssen,[2] a large amount of work has been done and a rather extensive literature has resulted. A summary of the earlier work, especially that concerning sugar hydrolysis, is given by Caldwell.[3] A discussion of later work, giving an account of some of the theories which have been proposed to explain this phenomenon, will be found in a recent paper by Bowe.[4] An excellent review of the present status of the problem is given by Schmid and Olsen.[5]

In recent years there have been many attempts made to explain the phenomenon in terms of the activity of the hydrogen ion in the reacting mixture, and the present view of several recent investigators is that the rate of decomposition of a compound by hydrogen or hydroxyl ion catalysis in salt solutions is related to the activity coefficients of these ions. Quali-

---

[1] This paper is an abstract of the thesis submitted by C. F. Kautz to the Graduate School of the University of Pittsburgh in partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

[2] Löwenthal and Lenssen, *J. prakt. Chem.*, **85**, 321 (1862).

[3] Caldwell, *Report Brit. Assoc. Adv. Sci.*, **1906**, p. 267.

[4] Bowe, *J. Phys. Chem.*, **31**, 297 (1927).

[5] Schmid and Olsen, *Z. physik. Chem.*, **124**, 97 (1926).

tatively, Åkerlöf[6] states that increase of the activity coefficient increases the velocity, and decrease of the activity coefficient decreases the velocity of the reaction in the case of hydrogen ion catalysis. References to a number of recent investigations illustrating this viewpoint are given by Åkerlöf in the article just quoted.

This investigation is an attempt to compare the rate of inversion of sucrose, using hydrochloric acid as the catalyst, in the presence of several univalent and bivalent chlorides, with the activity coefficients of the hydrogen ion in hydrochloric acid solutions containing the same salts. The activity coefficient data available in the literature are, however, for solutions not containing sucrose.

An empirical relation between the molar concentration of salt and velocity constant, proposed by Schmid and Olsen[5] as being of general application in describing the action of neutral salts in affecting hydrolytic reactions, has been tested with regard to its applicability to the inversion of sucrose. According to these investigators, the neutral salt action is described by the relation $K = K_0 \times 10^{rC}$, where K_0 is the velocity constant in the absence of salt, C is the concentration of added salt in moles per liter and r is an arbitrary constant.

Experimental Part

Materials.—The sucrose used in this work was of a pure commercial grade of cane sugar. It contained 0.05% of moisture and 0.005% of ash. It polarized 99.9° Ventzke at 20° and was considered to be of a sufficient purity for use in this work. It was kept in a desiccator over concentrated sulfuric acid.

Potassium, sodium, lithium, barium, calcium and strontium chlorides were used. The commercial c. p. grade was used and, with the exception of the lithium and calcium chlorides, they were purified by recrystallization three times from distilled water and were dried in an electric oven at 105–110°. The barium and strontium chlorides were dried at 120°, as at that temperature they lose completely their water of crystallization. The lithium and calcium chlorides were used in the form of concentrated solutions, which were standardized by determining chlorine as silver chloride.

Standard hydrochloric acid was prepared from constant boiling hydrochloric acid made according to the method of Foulk and Hollingsworth.[7]

Apparatus.—The saccharimeter used in this work was a Schmidt and Haensch triple field, Soliel-Ventzke type instrument.

The polarimeter tubes were 200 mm. long and were provided with metal jackets through which water was circulated from a thermostat. The tubes were provided with tubulures for thermometers.

The thermometers used were compared with a standard thermometer and corrections applied.

A 75-watt, 110-volt "Mazda" lamp was taken as the light source, the light being filtered through a 3 mc. layer of a 3% potassium bichromate solution.

Experimental Procedure.—The experiments were carried out in all cases using 20 g. of sugar to 100 cc. of solution. For each determination 50 g. of sugar and a quantity of

---

[6] Åkerlöf, This Journal, **48**, 3046 (1926).

[7] Foulk and Hollingsworth, *ibid.*, **45**, 1220 (1923).

the desired salt which when dissolved and diluted to 250 cc. would give the desired concentration, were accurately weighed and introduced into a calibrated 250cc. volumetric flask. In the case of the lithium and calcium chlorides the required amounts of the standardized solutions were added by means of a calibrated buret.

The sugar and salt were then dissolved in distilled water at 25.0°, allowing space for the addition of the hydrochloric acid. A quantity of standardized acid, also at 25.0°, was then added from a calibrated buret, such a quantity being taken that when filled to the mark the acid concentration was 0.100 N.

The solutions were thoroughly mixed and transferred to the polarimeter tubes and readings taken at different time intervals, the temperature being maintained at 25.0 ±0.05°. All readings were corrected for the "zero" reading of the instrument, which was frequently determined during the course of an experiment.

The flask containing the solution remaining after filling the polarimeter tubes was immersed in a thermostat at 25 ± 0.05°, for use in determining the final rotation. This final reading was taken at least forty-eight hours from the start of the reaction.

Method of Calculating Results.—The reaction velocity constants are calculated according to the ordinary monomolecular formula

$$K = \frac{1}{t} \log_{10} \frac{r_0 - r_\infty}{r - r_\infty}$$

where r_0 is the rotation at zero time, r is the rotation at a time t and r_∞ is the final rotation. Because of the experimental difficulties involved in directly determining initial rotations, and also because of the decrease in rotation of sucrose due to the presence of the salts, r_0 was indirectly determined using the method of Rosanoff, Clark and Sibley[8] and applying the method of least squares.

Results and Discussion

The results obtained in this investigation are given in Table I. The first column gives the molar concentration (moles per liter) of the salt, the second gives the experimentally determined velocity constant K, the third gives the ratio of the velocity constant to that obtained in the absence of salt and the fourth gives the $\log_{10} (K \times 10^4)$.

TABLE I

VELOCITY CONSTANTS FOR THE INVERSION OF SUCROSE WITH 0.100 N HYDROCHLORIC ACID IN THE PRESENCE OF NEUTRAL SALTS

Concn. of salt, moles/liter	$K \times 10^3$	K/K_0	$\log_{10} (K \times 10^4)$	Concn. of salt, moles/liter	$K \times 10^3$	K/K_0	$\log_{10} (K \times 10^4)$
0.000	0.430	1.00	0.6338				
	Potassium	Chloride			Barium	Chloride	
.050	.452	1.05	.6551	0.050	0.452	1.05	.6551
.100	.460	1.07	.6628	.100	.461	1.07	.6637
.200	.493	1.15	.6929	.200	.489	1.14	.6893
.500	.543	1.26	.7348	.500	.588	1.37	.7694
1.000	.648	1.51	.8116	1.000	.817	1.90	.9122
2.000	.962	2.24	.9832	1.300	.968	2.25	.9859
3.000	1.343	3.12	1.1281				

---

[8] Rosanoff, Clark and Sibley, THIS JOURNAL, 33, 1911 (1911).

TABLE I (*Concluded*)

Concn. of salt, moles/liter	$K \times 10^3$	K/K_0	$\text{Log}_{10} (K \times 10^4)$	Concn. of salt, moles/liter	$K \times 10^3$	K/K_0	$\text{Log}_{10} (K \times 10^4)$
	Sodium Chloride				Strontium Chloride		
0.050	0.472	1.10	.6739	.0050	0.500	1.16	.6990
.100	.485	1.13	.6857	.100	.533	1.24	.7267
.200	.506	1.18	.7042	.200	.568	1.32	.7544
.500	.547	1.27	.7380	.500	.649	1.51	.8122
1.000	.661	1.54	.8202	1.000	.959	2.23	.9818
2.000	.972	2.26	.9877	1.300	1.217	2.83	1.0853
3.000	1.492	3.47	1.1738				
	Lithium Chloride				Calcium Chloride		
0.050	0.460	1.07	.6628	.050	0.448	1.04	.6513
.100	.491	1.14	.6911	.100	.476	1.10	.6776
.200	.522	1.21	.7177	.200	.517	1.20	.7135
.500	.561	1.30	.7490	.500	.635	1.48	.8028
1.000	.676	1.57	.8300	1.000	.942	2.19	.9741
2.000	1.082	2.52	1.0342	1.300	1.188	2.76	1.0748
3.000	1.746	4.07	1.2420				

In each determination at least twelve readings were taken, at time intervals ranging from thirty minutes to two hours, the result given in the table being the average of these constants. In all the runs the average deviation from the mean was not more than 1%.

For comparison with the activity coefficients of the hydrogen ion in 0.100 *N* hydrochloric acid, containing similar amounts of these salts, use was made of the data of Harned[9] and Harned and Brumbaugh,[10] who have calculated, from electromotive force measurements, the activity coefficients for the hydrogen ion in 0.100 *N* hydrochloric acid containing various amounts of the chlorides of the metals used in this investigation. In order to obtain the activity coefficient and velocity constant data for comparable concentrations, it was necessary to convert the molal concentrations used by Harned to the molar basis. For the alkali chlorides Harned gives the concentrations expressed in both systems. In the case of the alkaline earth chlorides this conversion was effected by accurately making up from these salts a series of solutions in 0.100 *N* hydrochloric acid and determining their densities at 25.0° using a pycnometer.

In order to effect a comparison between the observed velocity constants and the activity coefficients of the hydrogen ion, the data are plotted as shown in Figs. 1 and 2. The abscissas, representing velocity constant and activity coefficient of the hydrogen ion, have been so chosen that starting the two sets of curves at a common point, the units selected represent equal percentage increases in the variables. The velocity

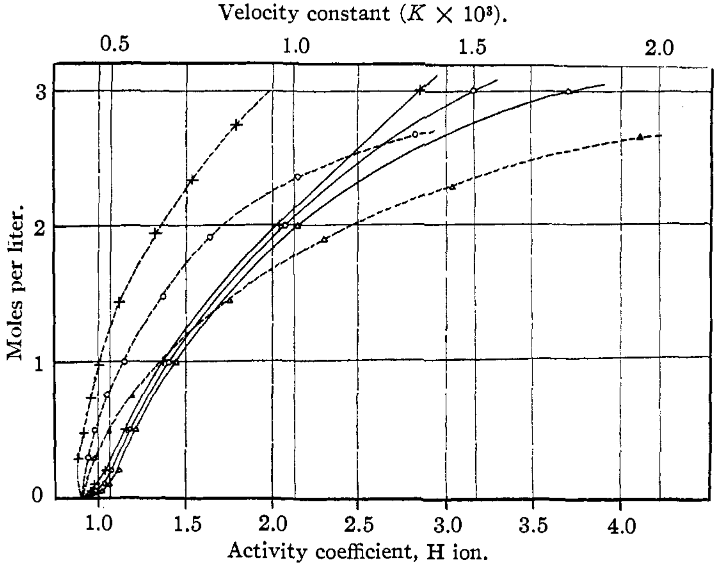
---

[9] Harned, THIS JOURNAL, **42,** 1808 (1920).

[10] Harned and Brumbaugh, *ibid.,* **44,** 2729 (1922).

constant curves are shown as solid lines and Harned's data, with concentrations expressed on the molar basis, are shown as broken lines.

Inspection of the curves indicates that there is no simple relationship between activity of the hydrogen ion, as determined in solutions containing no sucrose, and rate of hydrolysis. In the case of the alkali chlorides the curves are in the same order, but in the case of the alkaline earth chlorides, strontium chloride is an exception. It might be expected that this curve would lie between the barium and calcium chloride curves, whereas it is found that strontium chloride is more effective in increasing the rate of hydrolysis than either of these salts. However, it does not seem to be an exaggeration to say that the increase in the hydrolytic action of the hydrochloric acid roughly parallels the activity coefficient of the hydrogen ion in these acid-chloride mixtures. It has been shown by Corran and Lewis[11] that the activity of the hydrogen ion is affected by the presence of sucrose. This is further discussed by Corran[12] and by Scatchard,[13] who concludes that the uncertainty as to the activity of the hydrogen ion in solutions containing sucrose makes inconclusive the attempts to obtain a quantitative relationship between reaction velocity and hydrogen activity. But in acid-salt-sucrose mixtures, especially



+, KCl; O, NaCl; △, LiCl; - - - - - -, activity coefficient; ————, velocity constant.

Fig. 1.

---

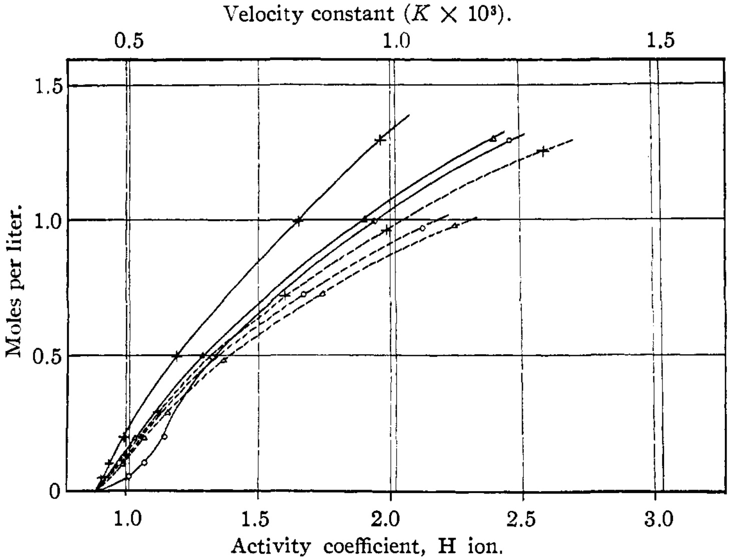
[11] Corran and Lewis, This Journal, **44**, 1673 (1922).

[12] Corran, *ibid.*, **45**, 1627 (1923).

[13] Scatchard, *ibid.*, **48**, 2026 (1926).

at high salt concentrations, there is no doubt that the effect of the salt on the hydrogen ion activity predominates over the sucrose effect, and there seems to be some qualitative agreement between our results and this conclusion.

According to Brönsted[14] the cane sugar inversion, which he formulates, $C_{12}H_{22}O_{11} + H_3O^+ =$, as a reaction between a neutral molecule and a univalent ion, shows a very small salt effect in dilute solutions and, furthermore, the effect is proportional to the salt concentration. At our lowest salt concentrations, 0.05, 0.10 and 0.20 *M*, we foundt his proportionality



+, $BaCl_2$; ○, $SrCl_2$; △, $CaCl_2$; ----, activity coefficient; ——, velocity constant.

Fig. 2.

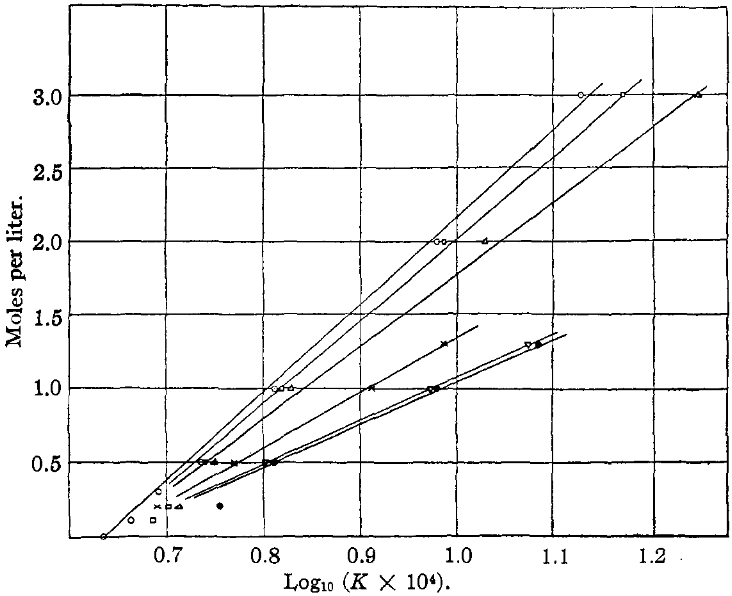
to exist only for the lithium chloride solutions. Certainly at higher salt concentrations the salt effect is not small (from 50 to 100% at 1 *M*). Brönsted states that the small, linear effect of salts like sodium chloride on the catalysis by hydrochloric acid in dilute solutions shows that the activity of the hydrogen ion is not the determining factor. This effect is evidence in favor of this theory of ionic reactions which postulates the formation of a "critical complex" by the reacting ions or molecules as the determining factor. Attempts to test the activity theory in strong salt solutions are not justified, he believes, because the changes of the solvent due to the great concentration of salt have obscured the simple activity

---

[14] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922), and "Contemporary Developments in Chemistry," Columbia University Press, 1927.

effect. Hückel's[15] extension of the theory of Debye and Hückel,[16] however, to concentrated solutions, taking into account in a formal way the effect of solvent changes on the activity coefficients of ions, seems to justify and encourage such a comparison.

If the dehydration of the H_3O^+ ions, or the displacement of the water equilibrium (equilibrium between mono-, di- and tri-hydrol) is the chief effect of the added salt,[4] then the various chlorides might be expected to influence the activity of the hydrochloric acid in the order of their hydration. The most recent data on the hydration of the alkali and alkaline earth chlorides[17] indicate that, of the alkali chlorides, lithium is the most strongly hydrated and potassium the least, which is in agreement with the order of their influence on the activity coefficient and hydrolytic action of the hydrogen ion. Strontium and calcium chlorides have practically the same hydration numbers up to 2 N; barium chloride is less hydrated.



○, KCl; □, NaCl; △, LiCl; ×, $BaCl_2$; ●, $SrCl_2$; ▽, $CaCl_2$.

Fig. 3.

Harned[18] has examined certain data of Rivett on the acid hydrolysis of chlorylacetanilide to *p*-chloro-acetanilide in the presence of salts, and in this case also strontium chloride shows a greater effect than calcium

---

[15] Hückel, *Physik. Z.*, **26**, 93 (1925).

[16] Debye and Hückel, *ibid.*, **24**, 185, 305 (1923).

[17] Sugden, *J. Chem. Soc.*, **129**, 174 (1926).

[18] Harned, This Journal, **40**, 1461 (1918).

or barium chloride. The data obtained by us show the accelerating effect of the salts to be of the same order as in the work quoted.

Curves are also plotted using molar concentration of salt as abscissas and the logarithm of the velocity constants as ordinates in Fig. 3. For agreement with the equation of Schmid and Olsen straight lines should be obtained. The equation holds fairly well for concentrations of salt above 0.5 M, particularly for the alkaline earth chlorides.

This equation seems derivable from the Hückel expression for the activity coefficient of an ion in concentrated solutions, with certain assumptions. The activity coefficient of the H$^+$ ion in 0.1 *N* hydrochloric acid is

$$\log \gamma_{H^+} = \frac{-a\sqrt{\mu}}{I + A\sqrt{\mu}} \qquad (1)$$

where *a* is a theoretical constant, *A* is a constant which depends on the mean distance of approach of the ions and μ is the ionic strength. The activity coefficient of the H$^+$ ion in concentrated solutions is, according to Hückel,

$$\log \gamma_{H^+} = \frac{-a\sqrt{\mu_s}}{I + A\sqrt{\mu_s}} + B\mu_s \qquad (2)$$

where μ_s is the ionic strength at the particular concentration of added salt and *B* represents the effect of the ions on the dielectric constant of the solvent. The activity of the H$^+$ ion at any concentration *C* (in these experiments 0.1 *N*) is

$$\log f_{H_0^+} = \frac{-a\sqrt{\mu_0}}{I + A\sqrt{\mu_0}} + \log C \qquad (3)$$

and the activity of the H$^+$ ion at the same concentration in the presence of other ions is

$$\log f_{H^+} = \frac{-a\sqrt{\mu_s}}{I + A\sqrt{\mu_s}} + B\mu_s + \log C \qquad (4)$$

If, at high concentrations, the change in the dielectric constant of the medium determines γ and f (the first term of the right side of (4)) is neglected in comparison with the second term, then the activity of the H$^+$ ion in strong salt solutions is related to the activity of the H$^+$ ion of the same concentration, but with no added salt, in this way

$$\log f_{H^+} - \log f_{H_0^+} = B\mu_s + \frac{a\sqrt{\mu_0}}{I + A\sqrt{\mu_0}} \qquad (5)$$

The second term of the right side of (5) is small for strong acids at low concentrations; dropping this term brings (5) into conformity with the equation of Schmid and Olsen, which may be written

$$\log K = \log K_0 + rC$$

Summary

The rate of inversion of sucrose by 0.100 *N* hydrochloric acid, at 25°, in the presence of potassium, lithium, sodium, calcium, strontium and barium chlorides of concentrations from 0.05 to 3 *N*, has been determined.

No simple relationship was found to exist between the increased rate of inversion in the presence of these salts and the activity coefficients of the hydrogen ion in solutions of the same acid and salt concentrations containing no sucrose, but the rough parallelism observed indicates that the activity of the hydrogen ion is probably the most important factor in determining the rate of inversion.

For concentrations of salt above 0.500 M an equation proposed by Schmid and Olsen as describing the neutral salt action, $K = K_0 \times 10^{rC}$, has been found to apply fairly well.

The equation of Schmid and Olsen is derived from the Hückel expression for the activity coefficient of an ion in concentrated solutions, with certain assumptions. This also indicates the importance of the activity of the hydrogen ion in determining the rate of inversion.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MCGILL UNIVERSITY]

A MICRO CALORIMETER

BY S. G. LIPSETT, F. M. G. JOHNSON AND O. MAASS

RECEIVED DECEMBER 28, 1927 PUBLISHED APRIL 5, 1928

In this paper is described a small calorimeter with which heats of solution may be determined using only 4 cc. of solvent and corresponding amounts of solute. The heat capacity of the calorimeter itself is approximately 1 calorie. The calorimeter in all its essential details resembles very closely a larger calorimeter which was developed in this Laboratory in connection with work on the surface energy of solid sodium chloride.[1]

For a complete description of the construction and manipulation of this type of calorimeter, the reader is referred to these two papers. The following brief description may, however, be given here. The calorimeter, which is cylindrical in shape and closed at both ends, is placed with its axis horizontal and is able to revolve on an axle at each end. A separate vessel inside the calorimeter contains the solute, this vessel being surrounded by the solvent. On rotation, the solute and solvent mix. The adiabatic method of calorimetry is used. The calorimeter is enclosed in a copper jacket and the whole submerged in a bath of water (about 14 liters). By means of a radiation thermel placed in the air space between the calorimeter and the copper jacket, the temperature of the bath of water is kept always at the same temperature as the calorimeter. The actual temperature of the calorimeter is then determined by means of a platinum resistance thermometer placed in the bath of water.

[1] (a) Lipsett, Johnson and Maass, THIS JOURNAL, **49**, 925 (1927); (b) Lipsett, Johnson and Maass, *ibid.*, **49**, 1940 (1927).