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The Activity Coefficients of Hydrochloric Acid in Aqueous Solutions Containing Either Sodium Dithionate or Perchloric Acid

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The effect of added salts upon the activity of hydrochloric acid has been studied by a number of investigators.[2] All of these, except Bates and Urmston,[2d] have employed chlorides for the added salts. In the present investigation the influence of the added electrolytes sodium dithionate and perchloric acid was studied, that is, the effect of a negative bivalent ion and that of hydrogen ion were determined. These salts are among the relatively few (except chlorides) which are suitable for this purpose.

The electromotive forces of cells of the type H_2, $HCl(m_1)$ + salt (m_2), $AgCl + Ag$ were determined at 25°. Except where noted the experimental procedures were similar to those of Bates and Urmston.[2d]

The sodium dithionate used was prepared by recrystallizing a C. P. product three times from water. It gave no turbidity with silver nitrate. The salt crystallizes as $Na_2S_2O_6 \cdot 2H_2O$. The proportion of water was determined at intervals and always checked very closely with the calculated value.

The perchloric acid solutions were prepared from the 60% C. P. product of the G. Frederick Smith Corp. It had been redistilled *in vacuo* and was stated to contain not more than 0.004% non-volatile matter. The acid gave no test for chlorides, sulfates or lower oxy-acids.

All mixtures were made up by weight from stock solutions and from solid salt. All concentrations are expressed as moles per 1000 g. of water.

That dissolved air has an effect upon the potential of the calomel electrode in acid solution due to a reaction between mercury, chloride ion, hydrogen ion, and oxygen, has been clearly demonstrated by Randall and Young.[3] The similar effect on the silver–silver chloride electrode is less serious. Güntelberg[2b] found some influence and removed oxygen from his solutions by means of nitrogen. Randall and Young, however, discovered no measurable effect upon silver–silver chloride spiral[4] electrodes in 0.1 *M* hydrochloric acid.

The change in the potential of the silver–silver chloride electrode due to the presence of oxygen is associated with the removal of chloride ion

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[2] (a) Harned, THIS JOURNAL, **38**, 1988 (1916); **42**, 1808 (1920); **48**, 326 (1926); (b) Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); (c) Randall and Breckenridge, THIS JOURNAL, **49**, 1435 (1927); (d) Bates and Urmston, *ibid.*, **55**, 4068 (1933).

[3] Randall and Young, *ibid.*, **50**, 989 (1928).

[4] Spiral electrodes may offer less silver surface and hence less opportunity for oxidation than do electrodes employing electrolytic silver crystals. The latter were used by Güntelberg and in this investigation.

from the solution in immediate contact with the electrode, and is proportional to the fractional change in the activity of the chloride ion. Hence, other factors remaining the same, it is especially noticeable at low chloride concentrations. The removal of the chloride is facilitated by high hydrogen-ion concentrations and therefore increases with increasing acid concentration. Thus with solutions 0.01 *M* in hydrochloric acid and 0.09 *M* in perchloric acid, a decrease of about 1 millivolt was observed when oxygen-free solution was substituted for one which had been in equilibrium with air. With solutions in which the chloride content was 0.1 *M* or greater, the effect was always less than 0.1 millivolt. Hence for those solutions in which the chloride concentration was 0.1 *M* or less, the Linhart type of cell, in which the whole solution is saturated with hydrogen, was employed. Hydrogen was bubbled through the cell for twenty-four hours before introducing the silver–silver chloride electrodes.

Further evidence that a reaction occurs between silver and hydrochloric acid in the presence of air was obtained by shaking a piece of bright silver wire with 0.5 *M* hydrochloric acid for twenty-four hours. At the end of that time the surface of the metal was covered with a characteristic coating of silver chloride which darkened upon exposure to light.

TABLE I

ELECTROMOTIVE FORCES AND ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID

Part A. Effect of Sodium Dithionate

HCl	$Na_2S_2O_6$ × 3	E. m. f.	Activity coefficient
0.1036[a]	0.0	0.3505	0.795
.1036	.0500	.3521	.771
.1035	.1000	.3531	.756
.1034	.2000	.3544	.738
.1031	.4000	.3557	.722
.1029	.6000	.3564	.714
.1027	.8000	.3565	.714
.1026	.9000	.3561	.720
.1023	1.0500	.3564	(.718)
.1023	1.0500	.3560	.723
.1023	1.1000	.3559	.725
.0500	0.0	.3861	.830
.04997	.0500	.3886	.791
.04991	.1500	.3911	.755
.04985	.2500	.3923	.738
.04973	.4500	.3931	(.728)
.04973	.4500	.3938	.718
.04963	.6500	.3944	.711
.04949	.8500	.3944	.713
.04919	1.4291	.3934	.733

Part B. Effect of Perchloric Acid

HCl	$HClO_4$	E. m. f.	Activity coefficient
0.02498	0.02498	0.40304	0.837
.04821	.04821	.37140	.802
.1493	.1493	.31631	.758
.2570	.2570	.28849	.756
.3732	.3732	.26741	.758
.4961	.4961	.25059	.819
.02143	.03730	.42084	.841
.02445	.07337	.38849	.802
.09885	.2995	.31855	.765
.1881	.5644	.28420	.793
.2482	.7447	.26771	.829
.00988	0.08985	.41072	0.806
.04005	.3604	.34159	.771
.07087	.6378	.31116	.790
.09994	.8995	.29060	.834

[a] The changes in hydrochloric acid concentration result from the water of crystallization present in the sodium dithionate crystals added.

Experimental Results

The measured values of the electromotive forces at 25° and the activity coefficients are given in Table I. For solutions containing sodium dithionate the activity coefficients were computed with the aid of the values for pure hydrochloric acid solutions[5] α_0 by means of the following relation

$$\ln \alpha/\alpha_0 = (F/2RT)\Delta E \qquad (1)$$

Here ΔE is the difference between the electromotive force of the cell containing hydrochloric acid m_1 molal and that containing both hydrochloric acid m_1 molal and added dithionate.

In the case of the perchlorate mixtures such a direct comparison with the values for pure hydrochloric acid solutions is not possible. For such solutions the activity coefficients α were calculated from the equation

$$E - E_0 = -(RT/F)\ln(m_1 + m_2)m_1\alpha^2 \qquad (2)$$

Here m_1 and m_2 are the molal concentrations of the hydrochloric and perchloric acids, respectively; E is the measured electromotive force of the cell containing both acids; E_0 the molal electromotive force for the hydrogen silver–silver chloride cell. Here it is taken as 0.2221 volt.[6]

In Table II the data are shown interpolated to round values of hydrochloric acid and of added electrolyte.

TABLE II

ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN PRESENCE OF ADDED SALTS

Ionic strength	Added $Na_2S_2O_6$ HCl molality 0.1	0.5	Added $HClO_4$ Ratio HCl : $HClO_4$ 1:1	1:3	1:9
0.1	0.796	0.791	0.800	0.804	0.809
.2	.757	.754	.769	.773	.780
.5	.722	.719	.761	.767	.773
.7	.714	.712	.779	.787	.792
1.0	.717	.714	.820	.828	.834

Discussion

In general, the results of this and similar investigations must, for the present at any rate, be considered chiefly from the empirical standpoint. On account of the physical complexity of the problem[7] and of mathematical difficulties[8] the treatment of pure electrolytes is, except for very dilute solutions, incomplete and the situation is more complicated in the case of mixtures. However, brief reference will be made to certain relations between the results of this and of other investigations.

In many mixtures of constant ionic strength μ, the activity coefficient α of hydrochloric acid has been found to be related to the concentration m of

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(5) Values which Randall and Young[3] have given for pure hydrochloric acid were used.

(6) Randall and Young.[3] Carmody [THIS JOURNAL, **54**, 188 (1932)] has recently arrived at the value 0.2223. Since the values used for the activity coefficients of pure hydrochloric acid are those of Randall and Young, their value of E_0 is employed. The effect of any uncertainty in the values of these investigators is to change all activity coefficients by a constant factor.

(7) Bjerrum, *Trans. Faraday Soc.*, **23**, 445 (1927).

(8) Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 350 (1928).

the acid in the mixture and to the activity coefficient α_0 of pure hydrochloric acid at the same ionic strength by the equation.[2a]

$$\log \alpha = \log \alpha_0 + k(\mu - m) \tag{3}$$

In Fig. 1 are plotted values of log α against those of m at various ionic strengths for the sodium dithionate and perchloric acid mixtures. The above equation demands a linear relation. It will be seen that this relation is closely followed by the dithionate mixtures and is approximately obeyed by the perchloric acid mixtures. The values for the latter mixtures, particularly in dilute solutions, are, however, subject to somewhat greater uncertainty so that for both added electrolytes equation (3) possibly holds within the experimental error. In the case of added sodium dithionate it would appear that k of equation (3) has the same value at different ionic strengths; however, the data are neither sufficiently numerous nor accurate to be certain of this.

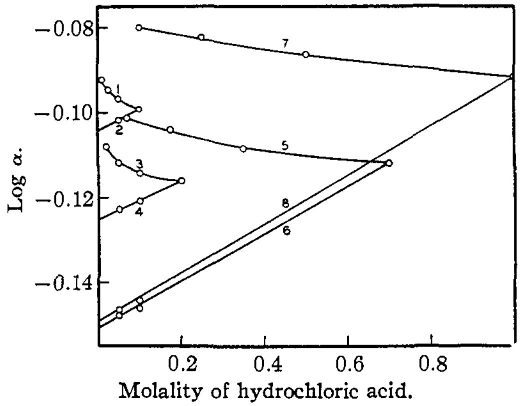

Fig. 1.—Added $HClO_4$: Curve 1, $\mu = 0.1$; Curve 3, $\mu = 0.2$; Curve 5, $\mu = 0.7$; Curve 7, $\mu = 1.0$. Added $Na_2S_2O_6$: Curve 2, $\mu = 0.1$; Curve 4, $\mu = 0.2$; Curve 6, $\mu = 0.7$; Curve 8, $\mu = 1.0$.

Equation (3) has been found to hold for dilute mixtures containing only univalent ions. The results of Randall and Breckenridge[2c] show that it is not followed by mixtures containing barium chloride or lanthanum chloride, but that the similar relation in which m, the concentration of the hydrogen ion constituent, is replaced by the geometric mean molality of the hydrogen and chloride ion constituents does hold. As these authors state, they give no derivation for this rule. Their relation does not hold for the data here presented for perchloric acid. Since equation (3) holds for sodium dithionate solutions, their rule does also, because for solutions containing no common ion the two relations are identical.

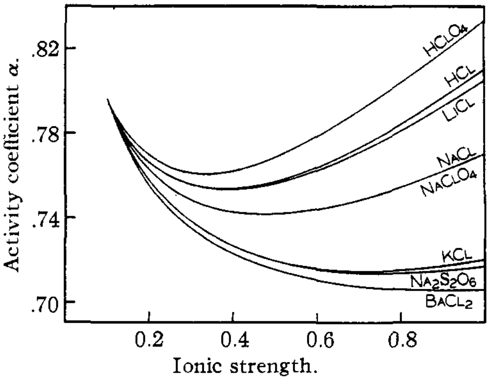

Fig. 2.—Effect of added salts upon 0.1 M HCl.

The comparative effect of increasing amounts of various salts upon the activity coefficient of hydrochloric acid is shown in Fig. 2. Here the activity coefficient of the acid, whose concentration is maintained constant at 0.1 *M*, is plotted against the ionic strength for the added electrolytes, lithium chloride,[2a] sodium chloride,[2a] potassium chloride,[2a] sodium perchlorate,[2d] barium chloride,[2c] sodium dithionate and perchloric acid. The figure shows that, as is to be expected, the minimum value for the activity coefficient is shifted most strongly to higher ionic strengths by those added salts which cause the greatest decrease in its value.

Of these added salts the activity coefficients of lithium chloride, sodium chloride, potassium chloride and barium chloride are known.[9] At a given ionic strength their activity coefficients decrease in the above order. Figure 2 shows that the effects of these salts on hydrochloric acid are in the same order. There is, however, no quantitative relation between the two sets of results. The comparative effects of sodium chloride and potassium chloride are somewhat anomalous since the activity coefficients of potassium chloride in its own pure solutions are but very slightly less than those of sodium chloride, while the activity coefficient of hydrochloric acid in the presence of the former is much less than in the presence of sodium chloride.

For those cases in which the activity coefficients of the salts in their own pure solutions are known, they are less, at the same ionic strength, than are those of hydrochloric acid in the mixture. From this it follows that the hydrogen ion has under certain conditions an unusually large tendency to escape from the solution. Thus, from the closely agreeing data of Harned[2a] and of Güntelberg,[2b] there may be found by extrapolation the activity product $\alpha_H\alpha_{Cl}$ in the solution 0.1 *f* NaCl + 0.0 *f* HCl. Taking the activity coefficient of 0.1 *f* HCl as 0.796 (Ref. 2) this product in 0.1 *f* NaCl is $(0.789)^2$. In this same solution the product $\alpha_{Na}\alpha_{Cl}$ has the value[10] $(0.778)^2$. Hence $\alpha_H/\alpha_{Na} = 1.03$[11] in 0.1 *f* NaCl. That is, the hydrogen-ion constituent has a greater tendency to be "salted out" from 0.1 *f* sodium chloride than has the sodium-ion constituent. This difference is associated with the fact that the electrical forces acting upon these two ions are not the same, though in both cases they are chiefly due to surrounding chloride ions. Thus the mean distances of the chloride ions will be different, for there are involved the diameters of the hydrogen and sodium ions, and the dielectric constant of the medium in their immediate neighborhood. In addition different proportions of these two ion constituents may exist as free ions. The fact that the hydrogen ion has a relatively large activity coefficient may be related to its simple structure. It is less deformable and less polarizable than other ions. The effect is to exert a greater repulsive force and the ion tends to escape from the solution.

(9) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., 1923, p. 362.

(10) Scatchard, THIS JOURNAL, **47**, 648 (1925).

(11) Due chiefly to uncertainties in the values for pure hydrochloric acid and pure sodium chloride solutions this figure may be about one per cent. in error.

We wish to acknowledge our indebtedness to Professor S. J. Bates of this Laboratory for much helpful advice and criticism during the course of this investigation.

Summary

The effects of added sodium dithionate and of added perchloric acid upon the activity coefficients of hydrochloric acid in aqueous solution were determined at 25° up to an ionic strength somewhat greater than unity.

The effects of these salts, which are of types not heretofore tested, are qualitatively the same as those of added chlorides of the alkali and alkaline earth elements. Thus, when added to a dilute solution of hydrochloric acid they cause its activity coefficient at first to decrease and then to increase with increasing ionic strength. The addition of perchloric acid increases the activity coefficient more than does that of any other electrolyte. In fact, the activity coefficient in these mixtures is greater than is that of pure hydrochloric acid at the same ionic strength.

The equation which has been found to hold for the effect of certain other electrolytes upon hydrochloric acid, namely, $\log \alpha = \log \alpha_0 + k(\mu - m)$ is closely followed by mixtures containing sodium dithionate and perchloric acid.

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The Rate of Addition of Methyl Esters to Trimethylamine[1]

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We have found that the rate of methylation of trimethylamine to tetramethylammonium ion by the methyl ester of a carboxylic acid is determined by the strength of the acid in a fashion which is without parallel in recorded ester reactions but is very similar to the general acid catalysis equation of Brönsted.[2] The reaction in question: $RCOOCH_3 + N(CH_3)_3 \longrightarrow RCOO' + N(CH_3)_4^+$, is of the same type as those upon which depend the familiar preparative use of the esters of strong acids as alkylating agents; in fact, now that the work of Hantzsch[3] has shown that those acids which are strong, and of equal strength, in aqueous solution are of very different inherent strengths, it becomes apparent that the useful alkylating agents are precisely the esters of the strongest acids, the sul-

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(1) This article is based upon a dissertation submitted by Helmuth L. Pfluger to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1933. The material was presented at the Washington Meeting of the American Chemical Society, March, 1933.

(2) Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924). See the review by Kilpatrick and Kilpatrick; *Chem. Rev.*, **10**, 213 (1932).

(3) Hantzsch, *Z. Elektrochem.*, **29**, 221 (1923).