Eucken and Mücke point out that with too high a frequency, the velocity of sound experiments on air and similar gases measures only a part of the vibrational energy. Kneser states that following a small and sudden change of pressure, each of the internal degrees of freedom, rotational and vibrational, requires a certain length of time to establish equilibrium with the translational degrees and that this time interval is a function of $h\nu/RT$. For a given temperature there is a critical frequency (or range of frequencies) below which the half period is relatively large and the particular internal degree is measured and above which the half period is too small for the degree to respond. For a given frequency and temperature, the internal degrees of freedom with relatively low $h\nu$ values will be measured and those with a relatively high $h\nu$ value will fail to respond. Due to the constancy of $C_v$ over such a large temperature range, it appears to be quite likely that both forms of dichloroethylene have three vibration degrees of freedom of such low frequencies that they respond fully, and that the other nine vibrations have such high frequencies that they do not contribute appreciably to the heat capacity below 250°.

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# The Activity Coefficients of Hydrochloric Acid in Aqueous Solutions Containing Either Sodium or Potassium Perchlorate

BY STUART J. BATES AND JOSEPH W. URMSTON

Recent investigations,[1] both theoretical and experimental, have emphasized the fact that except in very dilute solutions, activity coefficients of strong electrolytes cannot be accurately calculated from theoretical considerations alone.

The original Debye–Hückel development of the ion attraction theory showed that in dilute solution the activity coefficient is chiefly determined by the ionic strength. Its dependence upon other factors was later taken into account and more accurate formulas derived. These involve constants whose numerical values must be determined from the data themselves.[1d] One of these constants "$A$" is related to the ionic diameters. By making certain assumptions regarding its value in mixtures of electrolytes,

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[1] (a) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923); (b) Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924); (c) Noyes, *ibid.*, **46**, 1080, 1098 (1924); (d) Hückel, *Physik. Z.*, **26**, 93 (1925).

relatively simple relations between activity coefficients have been obtained.[2] The question as to the validity of such assumptions and relations must be settled by experiment.

Of the electrolytes which have been investigated at various activities, hydrochloric acid has been the most carefully and extensively studied, both in its own pure solutions and in mixtures. However, previous investigators[3] of mixtures have restricted themselves to adding salts containing the chloride ion. In this paper, and in that by Murdoch and Barton which immediately follows, the effects of other types of electrolytes, including those which contain no ion in common with those of hydrochloric acid, are described.

The activity of hydrochloric acid and hence the mean activity of its ion in salt mixtures may be computed from measurements of the electromotive forces of cells of the type

$$H_2\ (1\ \text{atm.}),\ HCl\ (m_1) + \text{salt}\ (m_2),\ AgCl + Ag$$

The quantities concerned are related by the equation

$$E - E_0 = -(2RT/F) \ln m_1\alpha \qquad (1)$$

Here $E$ is the measured electromotive force, $E_0$ the molal electrode potential, $\alpha$ the geometric mean activity coefficient of the ions of hydrochloric acid (more briefly, the activity coefficient of hydrochloric acid).

An added salt other than a chloride to be suitable for experiments of this nature must not react with the constituents of the cell and must possess certain other properties. Thus (1) it should be the salt of a strong acid, (2) the silver salt of its acidic constituent should be soluble, (3) it should not be the salt of an acid, like nitric acid, which may act as an oxidizing agent in solution and (4) it should be quite soluble. These conditions greatly restrict the choice of salts. However, sodium perchlorate appears to fulfil them admirably. Hence this salt was employed. In addition, in order to compare the relative effects of potassium and sodium ions, measurements were made employing potassium perchlorate; this salt is satisfactory except that it is not as soluble as could be desired.

## Experimental Procedure

The cells used consisted of three silver–silver chloride half cells and two hydrogen half cells, each of the latter containing two hydrogen electrodes. The half cells were connected through stopcocks.

The hydrogen electrodes were of platinum foil, first covered electrolytically with a thin coating of gold and then with one of platinum black. They were washed with nitric acid and then with many changes of water; they were kept in water until placed in the cell. The hydrogen electrodes prepared in this manner checked to 0.02 or 0.03 millivolt.

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[2] Harned, THIS JOURNAL, **48**, 326 (1926).

[3] (a) Harned, *ibid.*, **38**, 1986 (1916); (b) Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); (c) Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1927); (d) Randall and Breckenridge, THIS JOURNAL, **49**, 1435 (1927).

Electrolytic silver and precipitated silver chloride prepared from dilute solutions according to the directions of Randall and Young[4] were used for the silver–silver chloride electrode. These electrodes checked one another to 0.1–0.2 mv. The final results for the cells at various concentrations showed an average deviation from the smooth curve of not more than 0.15 mv.

The cells were in an oil thermostat regulated to 25 ± 0.05°. The electromotive forces were measured by the aid of a type K Leeds and Northrup potentiometer using as a standard a Weston cell that was frequently checked against a cell recently certified by the Bureau of Standards.

The hydrochloric acid was obtained by diluting a C. P. acid to a density of 1.1 and distilling in an all-glass still, which had been repeatedly employed for this acid distillation. Only the middle portion of the distillate was used; it was diluted to the desired concentrations, and these were checked by the silver chloride gravimetric method. The sodium perchlorate was prepared by the addition of perchloric acid of C. P. grade to a C. P. sodium carbonate, the product was twice recrystallized from water. Potassium perchlorate (C. P.) was purified by three crystallizations from water. Conductivity water was used in the preparation of all solutions.

Several series of measurements were made. In each series the electromotive force of the cell containing a solution of hydrochloric acid only was first determined. Then to weighed quantities of this solution were added weighed amounts of the pure dry salt and the electromotive forces of the cells containing these solutions were measured. In this manner any uncertainty due to errors of a constant nature may be minimized.

TABLE I

ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN SOLUTIONS OF CONSTANT ACID CONCENTRATION BUT VARYING SODIUM PERCHLORATE OR POTASSIUM PERCHLORATE CONCENTRATION

| $NaClO_4$ molality | E. m. f. | Activity coefficient |
|---|---|---|
| | HCl 0.2480 *M* | |
| 0.0 | 0.3078 | 0.760 |
| .1450 | .3086 | .749 |
| .2428 | .3089 | .744 |
| .2459 | .3088 | .745 |
| .5484 | .3079 | .759 |
| .7208 | .3070 | .772 |
| | HCl 0.1015 *M* | |
| 0.0 | 0.3513 | 0.795 |
| .0887 | .3537 | .761 |
| .1684 | .3543 | .750 |
| .3069 | .3548 | .743 |
| .5059 | .3548 | .743 |
| .6985 | .3542 | .752 |
| .8567 | .3534 | .765 |
| .8902 | .3532 | .768 |
| | HCl 0.04639 *M* | |
| 0.0 | 0.3899 | 0.833 |
| .01357 | .3907 | .820 |
| .03989 | .3920 | .798 |
| .0643 | .3931 | .783 |
| .0987 | .3938 | .771 |
| .1241 | .3944 | .763 |
| .2150 | .3953 | .750 |
| .2625 | .3957 | .745 |
| .2633 | .3956 | .744 |
| .2771 | .3957 | .745 |
| .3722 | .3959 | .741 |
| .4446 | .3961 | .739 |
| .4635 | .3961 | .739 |
| .6230 | .3955 | .747 |
| .8460 | .3946 | .760 |
| $KClO_4$ molality | E. m. f.<br>HCl 0.0994 *M* | |
| 0.0 | 0.3522 | 0.796 |
| .00714 | .3524 | .793 |
| .01318 | .3529 | .785 |
| .01720 | .3532 | .780 |
| .02476 | .3533 | .779 |
| .05864 | .3541 | .767 |
| .0884 | .3548 | .756 |
| .0981 | .3550 | .754 |
| .1219 | .3554 | .748 |

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[4] Randall and Young, THIS JOURNAL, **50**, 989 (1928).

The experimental results are given in Table I. All concentrations are expressed as moles per 1000 g. of water.

The effect of added salt upon the activity coefficient of hydrochloric acid may be readily computed for each series of experiments from the relation

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

Here $\Delta E$ is the difference between the electromotive force of the cell containing hydrochloric acid at the concentration $m_1$ and that of the cell containing hydrochloric acid at the concentration $m_1$ and in addition an added salt; $\alpha_0$ is the activity coefficient of the acid in the former solution, $\alpha$ its coefficient in the mixture.

Randall and Young[4] have made a careful study of all available data from which the activity coefficients of hydrochloric acid in its own pure solutions may be computed and have given a set of consistent values for 25°. We have taken our values for the pure solutions ($\alpha_0$) from their results and have then computed values for mixtures by means of the above equation. Such values interpolated to round values of the acid concentration and of ionic strength are given in Table II.

TABLE II

ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN SODIUM PERCHLORATE AND POTASSIUM PERCHLORATE MIXTURES OF CONSTANT IONIC STRENGTH

| Ionic strength | Pure HCl | HCl ($m$) + $NaClO_4$ | | | Ionic strength | Pure HCl | HCl (0.1 $m$) + $KClO_4$ |
|---|---|---|---|---|---|---|---|
| | | $m$ = 0.25 | $m$ = 0.10 | $m$ = 0.05 | | | $m$ = 0.10 |
| 0.1 | 0.796 | .. | 0.796 | 0.791 | 0.1 | 0.796 | 0.796 |
| .25 | .759 | 0.759 | .754 | .751 | .15 | .777 | .769 |
| .5 | .757 | .746 | .742 | .739 | .20 | .766 | .754 |
| .7 | .773 | .753 | .749 | .747 | | | |
| 1.0 | .810 | .776 | .770 | .767 | | | |

## Discussion

These results will be considered here chiefly with reference to a relation which may be[2] obtained from the ion attraction theory with the aid of the assumption that the ionic diameters of all ions present in the solution are the same. This relation [see also Brönsted, THIS JOURNAL, **45**, 2898 (1923)] which applies to solutions of constant ionic strength is as follows

$$\log \alpha = \log \alpha_0 + k(\mu - m) \qquad (3)$$

Here $\alpha$ and $m$ are the activity coefficient and molal concentration, respectively, of an electrolyte in a mixture of ionic strength $\mu$; $\alpha_0$ is its activity coefficient in its own pure solution of ionic strength $\mu$; and $k$ is a constant characteristic of both electrolytes.

Heretofore this relation has been tested only with salts containing the common chloride ion. Harned[3a] found this relation to hold closely for hydrochloric acid in the presence of added potassium, sodium or lithium chlorides at ionic strengths of 0.1, 1.0 and 3.0 molal; Hawkins[5] has shown

(5) Hawkins, THIS JOURNAL, **54**, 4480 (1932).

that the range for these three added chlorides extends to 6 molal. It holds less closely for sodium and potassium hydroxides in their corresponding chloride solutions at high ionic strengths.[6] Güntelberg[3b] determined the activity coefficients of hydrogen chloride in solutions of added lithium, sodium, potassium and cesium chlorides at an ionic strength of 0.1 molal. His results agree very closely with the requirements of the above equation.

In Fig. 1 are plotted for the ionic strengths 0.1, 0.25, 0.5, 0.7 and 1.0 the logarithms of the activity coefficients of hydrochloric acid in sodium perchlorate mixtures against concentrations *m* of the acid. The relations are linear, thus satisfying the requirements of equation (3). All of the lines have the same slope, namely, *k* = 0.0244. None of the points deviate from the linear relation by an amount corresponding to as much as 0.20 mv. In the same figure are plotted the corresponding values which Harned[2] obtained in this range of ionic strengths for the effect of added sodium chloride upon hydrochloric acid. These points lie along the same straight lines, thus showing that added sodium chloride and added sodium perchlorate have the same effects upon the activity coefficient of hydrochloric acid.

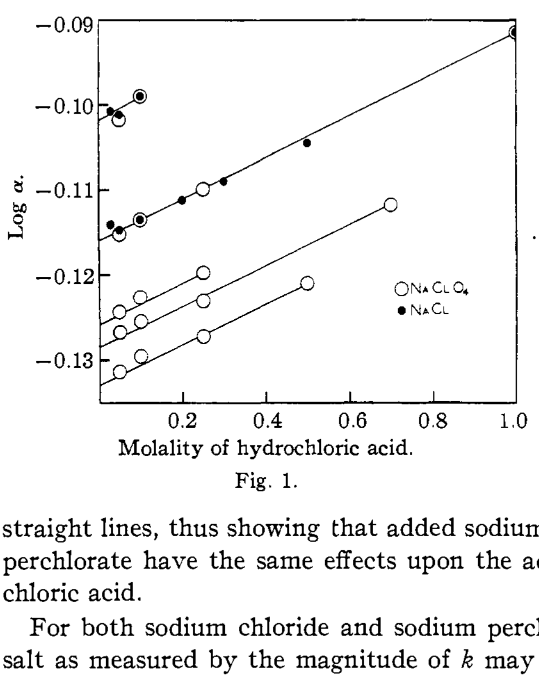

Fig. 1.

For both sodium chloride and sodium perchlorate the effects of added salt as measured by the magnitude of *k* may be somewhat greater at an ionic strength of 0.1 molal than at higher concentrations. Due in part to the small concentration range involved, the slope for this line is more uncertain[2] than that for the other series.

In agreement with the fact that added sodium chloride and sodium perchlorate have substantially the same effect upon the activity coefficients of hydrochloric acid, the few values obtained for the effect of added potassium perchlorate agree closely with those calculated upon the basis of the effect of added potassium chloride.[2] In each case the potassium salt has a greater effect than has the sodium salt.

It might be expected that because sodium chloride and sodium perchlorate have substantially the same effect upon hydrochloric acid, they would have the same effect upon other electrolytes. That this is not the

(6) Harned and Harris, THIS JOURNAL, **50**, 2633 (1928).

case is shown by the results of Bozorth,[7] who determined the effect of added salts including sodium chloride and sodium perchlorate on the solubility of potassium perchlorate. At an ionic strength of 0.5 molal he found that the activity coefficient of potassium perchlorate was about 7% greater in the presence of added sodium chloride than it was in the presence of added sodium perchlorate. It is thus seen that these effects are very specific and hence in general predictions cannot be made with any degree of confidence.

## Summary

The effect of added sodium perchlorate, an electrolyte without a common ion, upon the activity of hydrochloric acid at ionic strengths between 0.05 and 1.0 molal and at concentrations of acid from 0.05 to 0.25 molal has been determined by means of electromotive force measurements of the cell $H_2$, HCl ($m_1$) + $NaClO_4$ ($m_2$), AgCl + Ag.

The equation proposed by Harned for solutions of constant ionic strength $\mu$, namely, $\log \alpha = \log \alpha_0 + k(\mu - m)$, holds well for hydrochloric acid in the presence of added sodium perchlorate. The value of the constant $k$ is independent of the ionic strength.

Added sodium perchlorate has, within the range where comparisons are possible, quantitatively the same effect upon the activity coefficient of hydrochloric acid as does added sodium chloride. There is hence no essential difference upon the activity coefficient of hydrochloric acid, between the effect of a salt with a common ion and one without a common ion.

A few measurements were made employing potassium perchlorate as the added salt, but they could not be extensive because of its limited solubility. Within the concentration range investigated, potassium perchlorate has the same effect as has potassium chloride upon the activity of hydrochloric acid.

In general, however, all of these effects are quite specific.

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(7) Bozorth, THIS JOURNAL, **45**, 2653 (1923).