

## ACTIVITY COEFFICIENTS OF BISMUTH CHLORIDE IN HYDROCHLORIC ACID SOLUTIONS

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The concept of activity was introduced into the thermodynamics of solutions by Lewis. By calculations from conductivity measurements he found that solutions of strong electrolytes and even concentrated solutions of weak electrolytes do not obey the Oswald dilution law, and that such measurements do not give any definite information as to the actual ion activity in these solutions. In 1912 Lewis showed by thermodynamic treatment of existing data that in all cases the activity of the ions is very much less than the ion concentration calculated from conductivity data. The theory of complete ionization has been adopted by various authors<sup>2</sup> since then. It is now commonly accepted that the activity of strong electrolytes is influenced by the mutual attraction and repulsion of the ions in the solution.

The behavior of mixed electrolytes in the same solution has been investigated by several workers. Experiments have been carried out by Ming Chow<sup>3</sup> and Harned<sup>4</sup> dealing with the activity coefficient of hydrochloric acid in the presence of other chlorides, and it appears from these results that the activity coefficient of the acid depends upon the specific nature of the added chloride.

Since bismuth chloride hydrolyzes when it comes in contact with water, it is necessary that hydrochloric acid be used in making the solutions. As far as can be ascertained, no investigation has ever been reported concerning the activity coefficient of bismuth chloride in hydrochloric acid solution. Noyes, Hall, and Beattie<sup>5</sup> have shown from conductance measurements that the complex ions  $\text{BiCl}_4^-$  and  $\text{BiCl}_5^{2-}$  are present in large proportions in such solutions. Smith<sup>6</sup> has calculated from electromotive force measurements the relative activities of the bismuth ion in solutions of bismuth perchlorate in perchloric acid and has found that the activity varies considerably, depending upon both the perchlorate and hydrogen ion concentrations.

In this investigation the activity coefficient of bismuth chloride in hydrochloric acid was determined from electromotive force measurements at 25° C. on the cell  $\text{Bi}(\text{Hg})_x$  (two phase);  $\text{BiCl}_3(m_1)$ ,  $\text{HCl}(m_2)$ ;  $\text{Hg}$ ,  $\text{Hg}_2\text{Cl}_2$ . The acid concentrations were approximately 0.1, 0.5 and 1.0 mols per 1000 grams of water. The bismuth chloride concentrations varied between wide limits. (See Table I.)

### Theoretical

The observed electromotive force of the cell which was used is given by the expression

$$E = 0.2700 - E_0 - 0.01972 \log a_+ a_-^3. \quad (1)$$

<sup>1</sup> From a thesis presented by E. M. Hattox in 1933 in partial fulfillment of the requirements for the degree Master of Science.

<sup>2</sup> Bjerrum: *Zeit. Electrochem.* **24**, 321. 1918. Milner: *Phil. Mag.* **25**, 742. 1913. Ghosh: *J. Chem. Soc.* **113**, 149, 627, 790. 1918.

<sup>3</sup> Ming Chow: *J. Am. Chem. Soc.* **42**, 488. 1920.

<sup>4</sup> Harned: *J. Am. Chem. Soc.* **42**, 1808. 1920.

<sup>5</sup> Noyes, Hall, and Beattie: *J. Am. Chem. Soc.* **39**, 2526. 1917.

<sup>6</sup> Smith: *J. Am. Chem. Soc.* **45**, 360. 1923.

In this expression, 0.2700 is the molal electrode potential of the Hg, Hg<sub>2</sub>Cl<sub>2</sub>, Cl<sup>-</sup> electrode in the presence of air<sup>7</sup> and E<sub>0</sub> is to represent the molal electrode potential of the Bi, Bi<sup>+++</sup> electrode. The activities of the cation and anion are represented by a<sub>+</sub> and a<sub>-</sub> and these are related to the molalities, m<sub>+</sub> and m<sub>-</sub>, and the activity coefficients, s<sub>+</sub> and s<sub>-</sub>, by the relations

$$a_+ = m_+ s_+ \quad a_- = m_- s_- \quad (2)$$

Since the individual ionic activity coefficients cannot be determined separately, the mean activity coefficient, s, is to be used, and this is defined by the expression

$$s^4 = s_+ s_-^3 \quad (3)$$

As was mentioned above, the complex ion BiCl<sub>4</sub><sup>-</sup> is present in large amount in solutions of bismuth chloride in hydrochloric acid. The dissociation constant for this ion is written as

$$\frac{a_+ a_-^4}{a_1} = K \quad (4)$$

where a<sub>1</sub> shall represent the activity of the BiCl<sub>4</sub><sup>-</sup> ion. The chloride ion concentration is given as a first, but close, approximation by m<sub>-</sub> = ΣCl - 4ΣBi, and the bismuth ion concentration by m<sub>+</sub> = ΣBi - ΣBiCl<sub>4</sub><sup>-</sup>. Total concentration of Bi or Cl is represented by prefixing the summation sign. Using equations (3) and (4) and assuming that the monovalent complex ion has the same activity coefficients as the chloride ion, we obtain that the molality of the bismuth ion is given by

$$m_+ = \frac{K \Sigma \text{Bi}}{K + s^4 (\Sigma \text{Cl} - 4 \Sigma \text{Bi})^4}$$

The molality of the chloride ion is m<sub>-</sub> = ΣCl - 4ΣBi.

Substituting these values in equation (1), we have

$$0.2700 - E - 0.01972 \log (\Sigma \text{Bi}) (\Sigma \text{Cl} - 4 \Sigma \text{Bi})^3 = E' = E_0 + 0.01972 \log \frac{K s^4}{K + s^4 (\Sigma \text{Cl} - 4 \Sigma \text{Bi})^4} \quad (6)$$

The values for the left side of this equality can be calculated from the data of the experiments. These values are recorded in Table 1 as E'. On the right hand side of the equation appear two constants, E<sub>0</sub> and K, and a third constant, A, in the equality

$$\log s = \frac{-1.512 \sqrt{\mu}}{1 + A \sqrt{\mu}} \quad (7)$$

which was chosen because this expression was derived by Debye and Huckel to represent the change in the activity coefficient with change in ionic strength. This equation is valid for tri-uni-valent salts at not too large a concentration either in water or in water containing other ions of a different kind. The calculation of the ionic strength takes all the ions into consideration but the calculation of the coefficient -1.512 takes into consideration only the charge on the Bi<sup>+++</sup> and Cl<sup>-</sup> ions.

A similar calculation was made assuming the formation of the BiCl<sub>5</sub><sup>=</sup> ion. But the calculations do not agree with the observed results as is shown by the dotted line, (c), in Figure 1 along which the points for experiments 8 to 14 would fall, while the points for experiments 1 to 7 did not vary much to be

<sup>7</sup> Randall and Young: J. Am. Chem. Soc. 50, 989. 1928.

noticeable on the graph. Hence it appears rather conclusively that  $\text{BiCl}_4^-$  is the ionic species that is present rather than  $\text{BiCl}_5^-$ .

### Preparation of Materials

The materials used in this investigation were very carefully purified. The water was distilled from alkaline permanganate and from barium hydroxide, and was stored in glass stoppered pyrex bottles.

Bismuth trioxide was prepared as follows: commercial bismuth nitrate was dissolved in 8% nitric acid, concentrated nitric acid was then added and the bismuth nitrate was precipitated by cooling the solution to  $0^\circ\text{C}$ . This process was repeated three times, giving small, very pure crystals. These were dried and ignited to bismuth trioxide at a temperature of about  $500^\circ\text{C}$ . This method was found to give better results than precipitating the bismuth as the carbonate and then igniting to the oxide.

The mercury was washed with nitric acid and then distilled three times under reduced pressure in a current of air.

The calomel was prepared by electrolysis of constant boiling hydrochloric acid, using a current of 3 to 4 amperes between a mercury anode and a platinum cathode.<sup>8</sup>

The bismuth amalgam was prepared by electrolysis of a 0.3 molal solution of bismuth chloride, made from the pure bismuth trioxide and constant-boiling hydrochloric acid. Mercury was used as the anode, and a platinum wire as the cathode. Electrolysis was continued, using a current of 6 amperes, until the mercury was saturated with bismuth and an excess of metallic bismuth deposited on the surface of the amalgam. The amalgam and the solution above it were heated until the excess bismuth dissolved in the mercury and then allowed to cool slowly to room temperature. The saturated amalgam thus warmed and cooled had solid bismuth in equilibrium with it at room temperature. It was kept under the bismuth chloride solution used in the electrolysis.

Constant-boiling hydrochloric acid was prepared by the method of Hollingsworth.<sup>9</sup>

The bismuth chloride solutions were prepared by weighing the different ingredients. An amount of bismuth trioxide slightly less than that required for a saturated solution was weighed quickly on a watch glass and transferred to a pyrex bottle. A weighed amount of hydrochloric acid of the desired molality was then added until the volume was practically one liter. All the succeeding solutions of a series were made by successively diluting with definite weighed amounts of acid of known molality.

An ordinary H type pyrex cell was used for the electromotive force measurements. Connection was made to the potentiometer lead-in wires by means of a mercury filled tube sealed to the bottom of each compartment. The cell was filled with solution, mercury placed in the calomel compartment, and then a layer of calomel placed over the mercury. The bismuth amalgam was placed in the other compartment, care being taken to have solid bismuth crystals in contact with the amalgam in the cell. Both the calomel and bismuth amalgam had been washed several times with the solution to be used in the cell. The cell was placed in the thermostat and allowed to reach equilibrium, which was usually attained within five hours.

<sup>8</sup> Lipscomb and Hewlett: *J. Am. Chem. Soc.* **38**, 21, 1916.

<sup>9</sup> Hollingsworth: *J. Am. Chem. Soc.* **45**, 1220, 1923.

The thermostat for controlling the temperature of the cells was filled with finoil and was of the usual type. The temperature of the bath was maintained at  $25^{\circ}\text{C.} \pm .005^{\circ}$ .

Electromotive forces of the cells were measured with a Leeds and Northrup Type K Potentiometer.

### Discussion of Results

The electromotive forces of cells with different bismuth and chloride on concentrations are given in Table 1. These are the average of three and in some cases four good determinations. The electromotive forces for cells with the more concentrated bismuth chloride solutions were constant for more than a day, with a maximum deviation from the mean of less than  $\pm 0.1$  m.v. The cells with a bismuth chloride concentration below 0.001 molal had a deviation of about  $\pm 0.2$  m.v., and remained constant for not more than three to five hours.

Table 1.

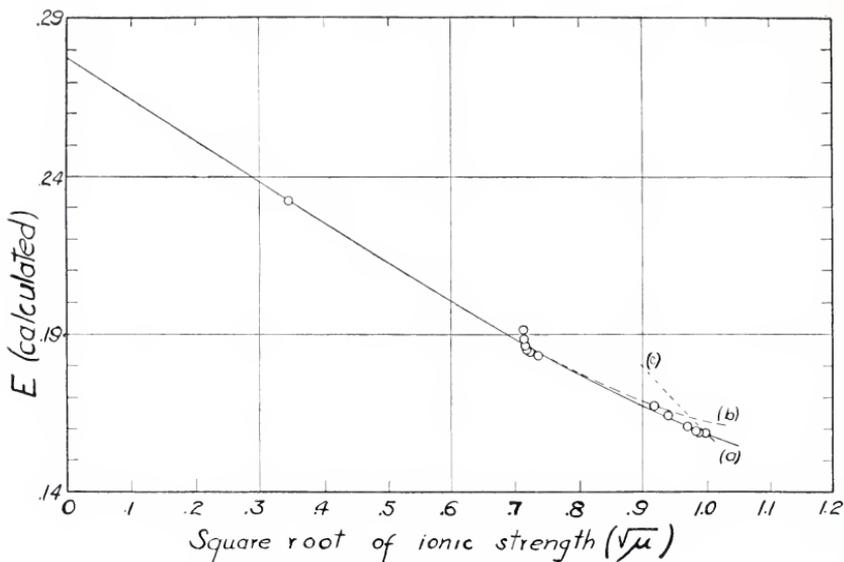
	$\Sigma\text{Cl}$	$\Sigma\text{H}$	$\Sigma\text{Bi}$	E(obs.)	E' eqtn. 6	log $\gamma$	$\sqrt{\mu}$
1	0.1191	0.1190	0.0000320	0.1810	0.2323	-0.5168	0.345
2	.508	.507	.000422	.1624	.1916		.712
3	.511	.509	.000781	.1600	.1887	-0.9638	.714
4	.515	.511	.00149	.1566	.1865	-1.0498	.715
5	.523	.514	.00298	.1519	.1851	-1.0877	.717
6	.541	.523	.00602	.1465	.1843	-1.1039	.723
7	.577	.541	.0121	.1410	.1831	-1.1232	.736
8	1.0054	.9986	.002252	.1632	.1591	-1.4477	.999
9	1.0070	.9925	.004820	.1575	.1585	-1.4611	.996
10	1.0038	.9760	.009264	.1520	.1590	-1.4562	.988
11	1.0100	.9688	.01373	.1485	.1594	-1.4512	.984
12	1.0110	.9399	.02370	.1432	.1612	-1.4261	.970
13	1.0127	.8851	.04254	.1369	.1643	-1.3855	.941
14	1.0126	.8415	.05700	.1333	.1674	-1.3417	.917

Table 2.

	E'	$\sqrt{\mu}$	$\Sigma\text{Cl} - 4\Sigma\text{Bi}$
1	0.1855	0.5218	0.5147
2	0.1616	.9300	.9088
3	0.2323	.3451	.1190

All the concentrations are expressed in mols per kilogram of water. The total chloride content is represented by  $\Sigma\text{Cl}$ , the total bismuth content by  $\Sigma\text{Bi}$ , and the total hydrogen ion content,  $\Sigma\text{H}$ , was obtained by subtracting  $3\Sigma\text{Bi}$  from  $\Sigma\text{Cl}$ , since  $\text{Bi}_2\text{O}_3$  was dissolved in the hydrochloric acid to prepare the solutions.

The electromotive forces, E', tabulated in column 5, Table 1, were calculated with the use of equation (6). These are plotted in Figure I as ordinates against the square root of the ionic strength as abscissas. The best values for the constants  $E_0$  and K in equation (6) and A in equation (7) were found by a trial and error method by requiring that equations (6) and (7) should satisfy exactly three selected points. The points chosen were: (1) the center of gravity of determinations 3-7, (2) the center of gravity of determinations 9-14 and (3) determination No. 1. The coordinates of these points are given in Table 2, and the resulting curve is represented in Figure I by the solid line marked (a). The dotted line marked (b) shows the variation when the constant K is not

Fig. 1. Calculated values of  $E'$  to determine  $E_0$ 

$2.9 \times 10^{-6}$  but  $2.2 \times 10^{-6}$ . The values for the other constants are  $E_0 = 0.2775$ ,  $A = 0.1$ . The best values for the constants are  $K = 2.876 \times 10^{-6}$ ,  $E_0 = +0.2771$ ,  $A = +0.0281$ . These constants were then used in equation (6) and the mean activity coefficient,  $\gamma$ , of bismuth chloride was calculated. These results are tabulated in column 6 of Table 1, and are also plotted in Figure II as the logarithm of  $\gamma$  against the square root of the ionic strength. The solid line curve in Figure II is calculated by the equation

$$\log \gamma = \frac{-1.512\sqrt{\mu}}{1 + 0.0281\sqrt{\mu}}$$

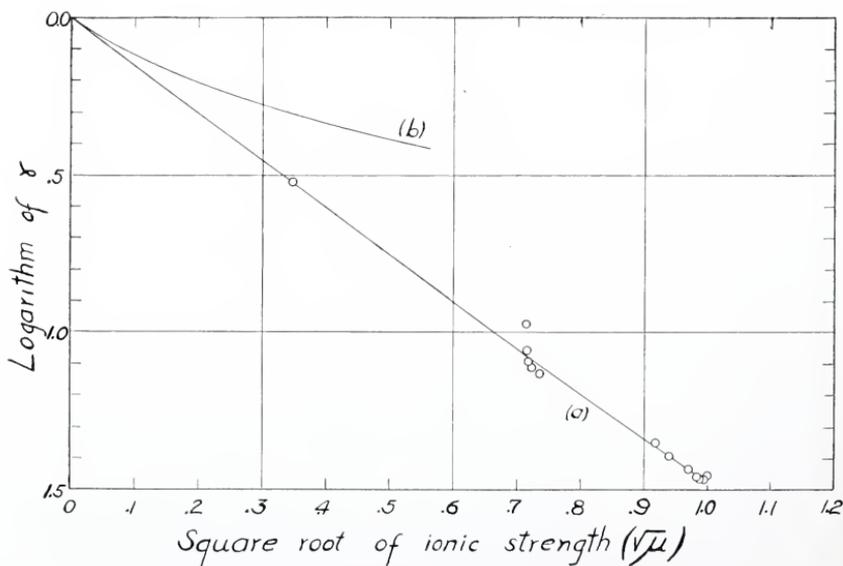


Fig. 2. Activity coefficients at different ionic strengths.

The values of  $S$  were calculated with the assumption that the activity coefficient of  $\text{BiCl}_4^-$  is the same as that of  $\text{Cl}^-$  (see equation 4). This is not necessarily true, hence any error introduced by this assumption appears in the calculated values of  $S$ , but with a percentage error only one-fourth as great. (Due to the fact that  $S^4$  appeared in the formulas.)

The curve marked (b) in Figure II shows how the logarithm of the activity coefficient for lanthanum nitrate varies with the ionic strength.<sup>10</sup>

The value of  $E_0 = 0.2771$  is to be taken as the molal electrode potential for the electrode  $\text{Bi}(\text{Hg})_x$  (two phase),  $\text{Bi}^{+++}$ , the sign of the potential being the sign on the electrode. Since in a two phase bismuth amalgam, bismuth is the solid phase, this is also the potential for  $\text{Bi}(s)$ ,  $\text{Bi}^{+++}$  electrode. Furthermore it is possible to calculate the molal electrode potential,  $E'_e$ , for the electrode  $\text{Bi}(s)$ ,  $\text{BiCl}_4^-$ ,  $\text{Cl}^-$ , from the equality

$$E'_0 + 0.01972 \log \frac{[\text{BiCl}_4^-]}{[\text{Cl}^-]^4} = E_0 + 0.01972 \log [\text{Bi}^{+++}]$$

The dissociation constant for  $\text{BiCl}_4^-$  has the value  $2.88 \times 10^{-6}$  from the data herein reported, hence the value for  $E'_0$  is  $+0.1678$ .

Other investigators have reported potentials for the bismuth electrode. Swift<sup>11</sup> reports for  $\text{Bi}(s)$ ,  $\text{BiO}^+$ ,  $\text{H}^+$  and for  $\text{Bi}(s)$ ,  $\text{BiOH}^{++}$ ,  $\text{H}^+$  the values  $+0.318$  and  $0.310$  respectively, whereas Smith<sup>12</sup> reports values of  $0.314$  and  $0.298$  for these two electrodes. Noyes and Ming Chow<sup>13</sup> worked with cells of the type  $\text{Pt}$ ,  $\text{H}_2$  (1 atm.),  $\text{HCl}$  (m),  $\text{HCl}$  (m) +  $\text{BiOCl}$  (s),  $\text{Bi}$  (s) and their results give a value  $E_0 = 0.1599$  for the  $\text{Bi}$  (s),  $\text{BiOCl}$  (s),  $\text{Cl}^-$  electrode.

### Summary

Cells of the type  $\text{Bi}(\text{Hg})_x$ , (two phase),  $\text{BiCl}_3$  ( $m_1$ ),  $\text{HCl}$  ( $m_2$ )  $\text{Hg}_2\text{Cl}_2$ ,  $\text{Hg}$  were studied at  $25^\circ$  at three different  $\text{HCl}$  concentrations and widely different  $\text{BiCl}_3$  concentrations. The results show that practically all the bismuth is in the solution as the complex ion,  $\text{BiCl}_4^-$ , with a dissociation constant of the order of magnitude  $2.88 \times 10^{-6}$ . The molal electrode potentials for the cells  $\text{Bi}$  (s),  $\text{Bi}^{+++}$  and  $\text{Bi}$  (s),  $\text{BiCl}_4^-$ ,  $\text{Cl}^-$  were determined to be  $0.277$  and  $0.1678$ . The mean activity coefficient for bismuth chloride in hydrochloric acid solutions with an ionic strength  $\mu$  is given by the formula

$$\log s = \frac{-1.512\sqrt{\mu}}{1+0.0281\sqrt{\mu}}$$

This assumed that the activity coefficient of the  $\text{BiCl}_4^-$  was the same as for the chloride ion.

<sup>10</sup> Lewis and Linhart: *J. Am. Chem. Soc.* **41**, 1951. 1919.

<sup>11</sup> Swift: *J. Am. Chem. Soc.* **45**, 37. 1923.

<sup>12</sup> Smith: *J. Am. Chem. Soc.* **45**, 360. 1923.

<sup>13</sup> Noyes and Ming Chow: *J. Am. Chem. Soc.* **40**, 739. 1918.