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The Stability Constants of the Stannous Bromide Complexes from 0 to 45° from Electromotive Force Measurements

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RECEIVED MAY 14, 1952

The stability constants for the complex species $SnBr^-$, $SnBr_2$, $SnBr_3^-$ and SnOHBr have been determined at 0, 25, 35 and 45°. The species $SnBr_4^=$ is not present in sufficient quantity to be determined in bromide concentrations up to 0.5 molar. All of the constants are smaller than the corresponding constants for stannous chloride complexes. The reactions forming stannous bromide complexes are less endothermal than the corresponding reactions for the stannous bromide system, but are accompanied by a considerably smaller increase in entropy.

The stability constants for the complex ionic species in stannous bromide solutions were first reported by Prytz,(1) who found them to be smaller than similar constants for the stannous chloride complexes. In recent kinetic studies Duke(2) reported the stability constant for formation of $SnBr^+$ to be 2.7, about one-fifth as large as that for the corresponding stannous chloride complex under the same conditions.

It seemed desirable to seek some explanation for this variation in terms of the heat of formation of the complex species. While these heats of formation cannot be determined with any high accuracy, nevertheless one can get some idea of their magnitude from the variation of the stability constants with temperature. Recent studies on cadmium chloride(3) and stannous chloride(4) complexes indicates that they are formed endothermally with a large entropy increase accompanying the process. This study was undertaken with the purpose of determining whether the smaller stability of the stannous bromide complexes was due to a more endothermal process of formation or to a smaller increase in entropy accompanying complex formation.

In this paper are presented the results of the study of the stability constants for stannous bromide complexes as determined from electromotive force measurements with concentration cells of the type

$$\mathrm{Sn(Hg)}\;\begin{array}{|l}\mathrm{Sn(ClO_4)_2\ (x)}\\ \mathrm{HClO_4\ (y)}\\ \mathrm{NaClO_4\ (3\text{-}x\text{-}y\text{-}z)}\\ \mathrm{NaBr\ (z)}\end{array}\;\begin{array}{||l|}\mathrm{Sn(ClO_4)_2\ (x)}\\ \mathrm{HClO_4\ (y)}\\ \mathrm{NaClO_4\ (3\text{-}x\text{-}y)}\\ \\ \end{array}\;\mathrm{(Hg)Sn}$$

in which the ionic strength is maintained constant at 3.0. The concentration units in the above cell are expressed in gram-equivalents per liter; since the concentration of stannous perchlorate was kept small, 0.01 mole per liter, the ionic strength was practically equal to the normality. Runs were carried out at different acidities and at four different temperatures, making possible a comparison of these stability constants with those obtained for the stannous chloride complexes under similar conditions by the same method.(4)

Experimental

The apparatus and procedure were the same as those used in the study of the stannous chloride complexes,(4) except for slight modifications in the cell and electrode assembly.

Solutions were prepared and handled under nitrogen as previously described. For this purpose, Matheson "pre-purified" nitrogen was further purified by the procedure of Meites and Meites.(5)

Solutions containing sodium bromide were prepared from J. T. Baker Analyzed sodium bromide, lot 1.2549, the analysis reporting 0.00% chloride ion. Before use the sodium bromide was carefully dried at 120° and stored in a desiccator. It was not sufficiently hygroscopic to introduce significant errors when weighing out portions. The sodium bromide was tested for the presence of bromates or oxidizing material by dissolving a portion in air-free water, adding potassium iodide, acidifying and testing with starch solution. No blue color appeared within two or three minutes with bromide concentration of about 1 *M*. Similar tests indicated the absence of oxidizing material in the perchlorate solutions.

Discussion

Treatment of Data.—Since the stannous concentration was kept low, only small changes in ionic strength were produced by complexing during each run. Under conditions of constant ionic strength, two assumptions are necessary. First, it is assumed that only a negligible junction potential will be produced as bromide ion is substituted for perchlorate ion at constant ionic strength, since the mobility of bromide ion is not much less than that of perchlorate ion. Second, the assumption is made that substitution of bromide ion for perchlorate ion at constant ionic strength will not appreciably change the activity coefficients of the species involved in the equilibria. The limitations of this assumption have been discussed in connection with the stannous chloride complexes(4); in general, the effects of this assumption will be small, particularly for the mono- and dibromo-complexes.

The equilibria between stannous and bromide ions are

$$\mathrm{Sn^{++}} + n\mathrm{Br^-} \rightleftarrows \mathrm{SnBr}_n^{2-n};\quad K_n = \frac{(\mathrm{SnBr}_n^{+2-n})}{(\mathrm{Sn^{++}})(\mathrm{Br^-})^n} \qquad (1)$$

described by the stability constants K_n, where n has integral values from 0 to 4 inclusive. The hydrolysis of stannous ion

$$\mathrm{Sn^{++}} + \mathrm{H_2O} \rightleftarrows \mathrm{SnOH^+} + \mathrm{H^+};\ K_\mathrm{h} = \frac{(\mathrm{SnOH^+})(\mathrm{H^+})}{(\mathrm{Sn^{++}})} \qquad (2)$$

is appreciable at low acidities, and the resulting $SnOH^+$ may associate with bromide ions to form mixed hydroxybromo-complexes

$$\mathrm{SnOH^+} + n\mathrm{Br^-} \rightleftarrows \mathrm{SnOHBr}_n^{+1-n};\ \delta_n = \frac{(\mathrm{SnOHBr}_n^{+1-n})}{(\mathrm{SnOH^+})(\mathrm{Br^-})^n} \qquad (3)$$

described by the equilibrium constants δ_n, where n has integral values from 0 to 3 inclusive.

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(1) M. Prytz, *Z. anorg. allgem. Chem.*, **172**, 147 (1928).

(2) F. R. Duke, THIS JOURNAL, **73**, 3048 (1951).

(3) E. L. King, *ibid.*, **71**, 309 (1949).

(4) C. E. Vanderzee and D. E. Rhodes, *ibid.*, **74**, 3552 (1952).

(5) L. Meites and T. Meites, *Anal. Chem.*, **20**, 948 (1948).

TABLE I

SUMMARY OF EXPERIMENTAL DATA[a]

Temp., °C.	0	0	25	25	25	35	45	45
Acid concn., M	0.5	0.15	0.5	0.25	0.1	0.5	0.5	0.15
No. of runs	1	1	5	2	3	1	1	1
Total bromide equiv./liter	E.m.f., millivolts							
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
.02	0.97	0.97	1.30	1.30	1.29	1.42	1.57	1.53
.05	2.42	2.41	3.25	3.24	3.21	3.58	3.91	3.79
.10	4.80	4.75	6.40	6.41	6.30	6.98	7.72	7.57
.15	7.18	7.07	9.52	9.50	9.30	10.33	11.41	11.19
.20	9.53	9.35	12.51	12.48	12.25	13.57	14.96	14.60
.25	11.85	11.55	15.42	15.35	15.10	16.67	18.36	17.89
.30	14.15	13.75	18.20	18.10	17.85	19.65	21.58	21.00
.40	18.55	17.95	23.40	23.23	23.00	25.20	27.51	26.70
.50	22.65	21.90	28.20	28.00	27.77	30.16	...	..
	Constants for equation 4							
A_1	4.30	4.34	5.37	5.37	5.33	5.71	6.11	5.96
A_2	8.60	7.65	13.2	13.0	12.1	14.9	17.5	16.0
A_3	15.5	12.6	21.3	19.7	18.8	23.0	27.4	24.3

[a] For all runs the ionic strength was 3.0 and the Sn^{II} concentration was 0.01 molar. All bromide concentrations refer to the total concentration at the temperature of the run.

In these expressions the symbols in parentheses are used to represent concentrations, and the "concentration constants" K_n, K_h and δ_n represent the products of the true equilibrium constants and an activity coefficient factor which is assumed to be constant under the experimental conditions used.

The electromotive force of the concentration cell is related to the concentration of the uncomplexed bromide ion by the expression

$$\exp(2FE/RT) = f^0 = \sum_{0}^{4} A_n(\mathrm{Br}^-)^n \qquad (4)$$

in which

$$A_n = [K_n + \delta_n K_{\mathrm{h}}/(\mathrm{H}^+)]/[1 + K_{\mathrm{h}}/(\mathrm{H}^+)] \qquad (5)$$

and in which, by definition, $A_0 = 1$ and $\delta_4 = 0$.

Equation 4 requires knowledge of the free or uncomplexed bromide ion concentration. The calculation of the uncomplexed bromide ion concentration from the experimental data is made through the relation

$$(\mathrm{Br}^-) = (\mathrm{Br}^-)_t - (\mathrm{Sn}^{++})_t \times \left(\frac{2F}{2.3026RT} \times \frac{\mathrm{d}E}{\mathrm{d}\log(\mathrm{Br}^-)_t} \times \frac{\mathrm{d}\log(\mathrm{Br}^-)_t}{\mathrm{d}\log(\mathrm{Br}^-)}\right) \qquad (6)$$

In practice, $\mathrm{d}\log(\mathrm{Br}^-)_t/\mathrm{d}\log(\mathrm{Br}^-)$ is very nearly equal to unity, so that by measuring the slopes of a plot of E against $\log(\mathrm{Br}^-)_t$, a very good approximation to (Br^-) can be computed from equation 6. From these values it is an easy matter to determine the small correction factor $\mathrm{d}\log(\mathrm{Br}^-)_t/\mathrm{d}\log(\mathrm{Br}^-)$ and then to compute a very good second approximation to (Br^-). The difference between the two approximations for these low values of stannous ion was of the order of 1 part per thousand.

Interpretation of Data.—A summary of the observed e.m.f. data is presented in Table I for rounded values of total bromide concentrations, taken from large scale graphs of E against $(\mathrm{Br}^-)_t$. The tabulated values of E represent the original data to 2 parts per thousand or better, while the reproducibility of the data as determined from duplicate runs was of the order of 5 parts per thousand.

Determination of the constants A_n was made using the method proposed by Leden,[6] which has also been used by deFord and Hume[7] in treating polarographic data. Constants for some of the runs were also determined by application of the method of least squares.[8] Good agreement was found between values computed by the two different methods. The method of Leden (a limiting slope of chord method) gives somewhat more weight to the data at low bromide concentrations in determining A_1, while in determining A_3 it gives more weight to the data at higher bromide concentrations, and is somewhat more desirable for these reasons. The values reported in Table I are those obtained by application of Leden's method.

As in the case of the stannous chloride complexes,[4] three constants A_1, A_2 and A_3 adequately represent the data for any run. At 45°, using the method of least squares, small values could be obtained for A_4, but these values were very sensitive to small variations in e.m.f. in the upper and lower ranges of bromide concentration, and were not considered sufficiently reliable to include in Table I. About all that could be established was that A_4 lay somewhere between 0 and 10 at 45°.

The variation of the constants A_n with acidity closely paralleled that observed in the study of the stannous chloride complexes,[4] indicating that in this case also there would be no mixed complexes containing more than one bromide ion, that is, δ_2 and δ_3 essentially are equal to zero. The values of K_{h} computed from the variation of A_2 and A_3 with acidity at each temperature agreed well with those found in the previous study.[4] Both sets of values were plotted against temperature, and the smoothed values reported in Table II were used in computing the values of δ_1 for the hydroxybromostannous complex from the variation of A_1 with acidity. While the uncertainties in K_{h} and δ_1 are rather large, the

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[6] I. Leden, *Z. physik. Chem.*, **A188**, 160 (1941).

[7] D. D. deFord and D. N. Hume, THIS JOURNAL, **73**, 5321 (1951).

[8] G. J. Cox and M. C. Matuschak, *J. Phys. Chem.*, **45**, 362, 369 (1941).

TABLE II

SUMMARY OF STABILITY CONSTANTS

	0°	25°	35°	45°	Average deviation
K_h	0.015	0.020	0.023	0.025	±0.004
δ_1	4.6	5.0	4.8	4.8	± .4
K_1	4.30	5.38	5.75	6.16	± .05
K_2	8.9	13.9	15.6	18.6	± .3
K_3	15.4	22.1	24.1	28.6	±1.5

errors introduced through this source in computing K_1, K_2 and K_3 from A_1, A_2 and A_3 are naturally quite small. In Table II the uncertainties indicated are estimated deviations based on the closeness with which the data could be fitted to equation 4 and upon the agreement between runs under the same experimental conditions.

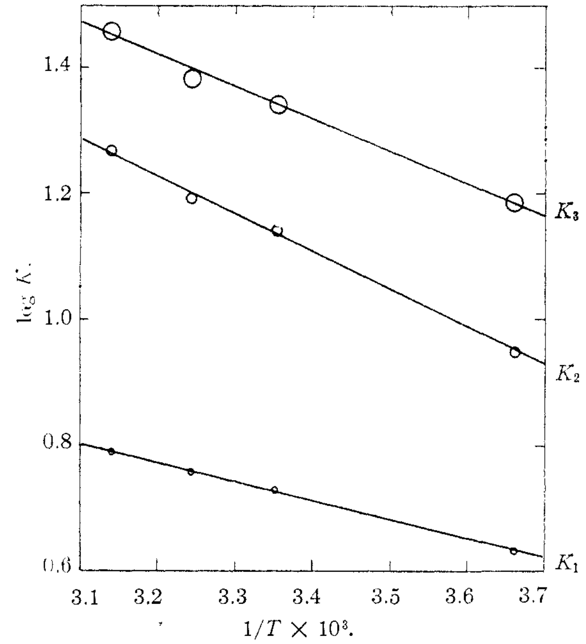

Fig. 1.—Variation of stability constants with temperature.

When the logarithms of the stability constants are plotted against the reciprocal of the absolute temperature, as shown in Fig. 1, the deviations of the points from the straight lines were less than the deviations given in Table II.

Changes in heat content, free energy and entropy for formation of the complexes are summarized in Table III. These quantities refer to the reactions occurring at ionic strength 3.0 (in sodium perchlorate as inert salt), rather than the usual standard states, and will contain the uncertainties due to the variation of the activity coefficient factors with temperature, which are probably no greater than the observed uncertainties.

TABLE III

FREE ENERGY, HEAT CONTENT AND ENTROPY CHANGES AT 25° FOR THE REACTION $Sn^{++} + nBr^- = SnBr_n^{+2-n}$

Complex formed	ΔF, cal./mole	ΔH, cal./mole	ΔS, cal./deg./mole
$SnBr^+$	−995 ± 10	1380 ± 50	8.0 ± 0.2
$SnBr_2$	−1555 ± 25	2730 ± 100	14.4 ± 0.4
$SnBr_3^-$	−1825 ± 50	2365 ± 250	14.1 ± 1.2

These data show that the stannous bromide complexes are formed less endothermally than the corresponding chloride complexes,[4] which would point to a higher stability for the bromide complexes. However, the bromide complexes are formed with much smaller increases in entropy than the chloride complexes; for this reason, the stability constants of the bromide complexes are actually the smaller. It is hoped that further studies on other systems now in progress in this Laboratory will reveal whether this entropy behavior is a characteristic difference between bromide and chloride, or whether it is partly dependent on the metallic ion.

Acknowedgment.—The author wishes to express his appreciation to the University of Nebraska Research Council for a Research Grant under which a portion of this work was carried out.

LINCOLN, NEBRASKA