XXXIV.—*The Colour and Constitution of Bromine Solutions.*

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IF a soluble bromide is added to bromine water, the colour of the solution is greatly diminished, the effect depending to some extent on the amount of bromide added, and it was thought that a quantitative examination of such colour changes might afford additional evidence for the constitution of bromine solutions which has been adduced from the study of their other properties. The experiments of Worley (*Trans.*, 1905, **87**, 1107) confirmed the views of previous workers, that a considerable part of the bromine was in the form of tribromide, and he found values for the dissociation constant in the equation:

$$k(\text{KBr}_3) = (\text{KBr}) \times (\text{Br}_2)$$

varying from 0.03 to 0.07, the variation being probably due to the presence of a portion of the bromine in the form of pentabromide.

The experiments recorded in this paper have led to a similar result, and have been extended to sodium bromide and hydrobromic acid; the presence of the compounds NaBr_3 and HBr_3 is similarly to be inferred, the dissociation constants of these being practically the same as that of the compound KBr_3 .

The method adopted consisted of finding the strengths of bromine and bromine-bromide solutions having the same intensity of colour.

Experiments with the colorimeter on bromine solutions are complicated by rapid loss of bromine from the surface when contained in an open vessel, and consequent lack of homogeneity of the liquid. It is essential that the liquid should be contained in a covered vessel which it completely fills, to enable concordant results to be obtained.

In comparing colours of the solutions, it was thus difficult to use standard bromine solutions the depth of which could be varied at will, and it became necessary to work with a third non-volatile substance, first with bromine water and then with bromine in potassium bromide; in this way, a relation could be obtained between the two latter.

A Duboscq colorimeter was used for the comparisons. In this instrument good diffused daylight reflected from a porcelain plate passes up through two vessels containing the liquids to be compared. A hollow glass cylinder closed at both ends dips into the standard

liquid, and by moving this up or down, the thickness of the layer of liquid between the bottoms of the containing vessel and hollow cylinder can be varied and read off on a scale. The two beams of light, after passing through the liquids, are reflected by prisms so as to illuminate the two halves of the field of an eye-piece.

FIG. 1.

The non-volatile substance used was potassium dichromate, which was chosen on account of the ease with which standard solutions are prepared and kept, and because it can be well matched against bromine.

The standard solutions of dichromate used were $2N$, N , $N/2$, $N/5$, and $N/10$. These are optically equivalent, that is, 4 cm. of a $N/2$ -solution are matched by 1 cm. of a $2N$ -solution, etc.

Bromine and potassium dichromate are not, however, optically equivalent. Their absorption spectra differ, that of the bromine extending further into the red, and ending much less sharply than that of dichromate. Further, if two oblong vessels be filled with bromine and dichromate respectively, so that the colours match when viewed through their long dimensions, the bromine appears far lighter when viewed through their short dimensions.

It has been found that this does not affect the final result, the dichromate being only introduced at an intermediate stage in order to effect comparison between the two bromine solutions.

The first part of the work consisted of comparing the colour of aqueous bromine of various strengths with potassium dichromate solutions, and from the results constructing a calibration curve by plotting strengths of bromine as abscissæ against cm. of $N/10$ -dichromate as ordinates.

Calibration Curve Showing the Relation between the Strength of Bromine contained and the depth in cm. of $N/10$ -Dichromate equivalent in colour.

The bromine was contained in a glass vessel about 2.7 cm. diameter and 1.7 cm. high, the top edge being ground and covered by a clear glass disk. The volume of the vessel was found by weighing to be 9.5 c.c.

The cell was filled with bromine water, and the colour matched with suitable dichromate. It was then dropped into potassium iodide, and the liberated iodine titrated with standard thiosulphate, whereby the molecular concentration of the bromine solution was determined.

TABLE I.
Construction of Calibration Curve.

Standard bi-chromate used.	Colorimeter readings.	Mean.	Colour of di-chromate in cm. $N/10$.	Molecular concentration of bromine water.
$N/10$	1.18, 1.20, 1.20, 1.13, 1.14, 1.18	1.17	1.17*	0.0122
$N/5$	1.16, 1.16, 1.17, 1.13, 1.18, 1.15	1.16	2.32	0.0177
$N/5$	2.25, 2.19, 2.25, 2.18, 2.26, 2.24	2.23	4.46	0.0261
$N/2$	1.47, 1.46, 1.41, 1.36, 1.45, 1.49	1.44	7.20	0.0323
$N/2$	1.60, 1.68, 1.64, 1.69, 1.55, 1.62	1.63	8.18	0.0347
N	1.39, 1.28, 1.39, 1.43, 1.40, 1.46	1.39	13.9	0.0464
N	2.14, 2.01, 2.02, 2.08, 2.01, 2.04	2.05	20.5	0.0556
$2N$	1.58, 1.56, 1.50, 1.67, 1.55, 1.50	1.56	31.2	0.0689
$2N$	1.75, 1.70, 1.67, 1.80, 1.75, 1.65	1.72	34.4	0.0720
$2N$	2.10, 2.11, 2.06, 2.04, 1.99, 2.18	2.09	41.8	0.0758
$2N$	2.78, 2.56, 2.83, 2.64, 2.56, 2.81	2.70	54.0	0.0845

* The mean multiplied by ten times the normality factor gives the colour in cm. of $N/10$ -dichromate.

The last two columns plotted give the calibration curve shown in Fig. 1 (p. 275).

Comparison of the Strengths of Solutions of Bromine in Water and in Aqueous Potassium Bromide, having the same colour.

A solution of bromine in potassium bromide solution of the required strength was placed in the cell and matched against a suitable dichromate solution. By means of the calibration curve, the strength of bromine water having the same colour was read off, and this was taken as the colour of the bromine-bromide solution, the unit of colour being that of aqueous bromine containing 1 gram-molecule per litre. The concentration of the bromine in the solution under examination was determined as before with potassium iodide and standard thiosulphate.

Only the mean of the colorimeter readings is given here, the agreement being of the same order as that shown by the calibration figures. At least six readings were made for each determination.

TABLE II.

Influence of Potassium Bromide on the Colour.

Molecular concentration of potassium bromide.	Standard dichromate used.	Mean colorimeter reading.	Colour expressed in strength of Br ₂ (from the calibration curve).	Bromine concentration (from the titration).
0.1	N/10	1.83	0.015	0.0255
0.1	N/5	1.29	0.018	0.0305
0.1	N/2	2.12	0.040	0.0620
0.1	N	1.51	0.0485	0.0712
0.1	2N	1.94	0.075	0.1071
0.4	N/5	2.58	0.027	0.0665
0.4	N/2	1.18	0.029	0.0708
0.4	N	1.09	0.041	0.0984
0.4	N	1.77	0.053	0.1239
0.4	2N	0.98	0.056	0.1305
0.4	2N	2.26	0.0785	0.1835
1.0	N/5	1.34	0.018	0.0547
1.0	N/2	1.05	0.027	0.0839
1.0	2N	0.45	0.037	0.1062
1.0	2N	1.10	0.0585	0.1811
1.0	N	2.13	0.0575	0.1830
1.0	2N	1.57	0.069	0.2060
1.0	2N	2.10	0.0765	0.2362
1.0	2N	2.38	0.0795	0.2592

The last two columns are plotted in Fig. 2, the colour of bromine water being shown as a straight line with equal ordinates and abscissæ.

A vertical line drawn across the diagram gives the colours of solutions having the same bromine concentration, and the numbers so obtained show the effect of increasing the concentration of the

potassium bromide on the colour of a bromine solution of fixed strength.

Thus, at line 1, where concentration of bromine is

0.1, when the conc. of KBr is 0.1, 0.4, 1.0
the colour is 0.07, 0.0415, 0.034,

FIG. 2.

and at line 2, where concentration of bromine is

0.05, when the conc. of KBr is 0.1, 0.4, 1.0
the colour is 0.032, 0.02, 0.016.

These numbers indicate clearly that whilst the addition of a small quantity of bromide causes a very marked falling off in the intensity of the colour, continued addition produces far less effect, and after

the concentration of potassium bromide has reached about 0.8, further addition produces little change.

As a further example, a solution of 0.204 molecular proportion of bromine in *N*-potassium bromide had a colour 0.065, whilst in 2*N*-potassium bromide the colour was 0.062; doubling the concentration of the bromide has thus little effect on the colour.

Colour change in solution may be caused by increase or decrease of electrolytic dissociation or change in constitution (compare Sidgwick and Tizard, *Trans.*, 1908, **93**, 187).

Since Jakowkin (*Ber.*, 1897, **30**, 518) found that bromine water cannot be ionised to any considerable extent, the addition of a soluble bromide could hardly increase its dissociation.

A few experiments were made with the view of determining the effect of the addition of bromine on the conductivity of potassium bromide solutions, and it was found that at 25° the addition to 0.4*N*-potassium bromide of 0.2 gram-molecule of bromine per litre lowers its conductivity about 8 per cent., 0.2 gram-molecule per litre of the non-electrolyte sugar lowering it about 12 per cent. The lowering may be due to viscosity changes, and is in harmony with the view that no great change in ionic concentration is caused by the addition of the bromine.

The colour changes must therefore almost certainly be due to some change of constitution, the simplest of which would be the formation of the compound KBr_3 .*

In the simple treatment that follows, it is assumed that the limit of colour change is reached in normal potassium bromide solution. It is further assumed that potassium tribromide is the only additive compound the presence of which need be considered.

If, then, after this concentration has been reached, further addition of potassium bromide produces no effect, the whole of the bromine must be in the combined state, and the colour of the solution in *N*-potassium bromide (within the limits of bromine concentration here dealt with) is due to potassium tribromide, and not to free bromine.

Consider a solution of bromine in potassium bromide, the total concentration of the dissolved bromine being α . Let its colour be C . Further, let the colour of a solution of potassium tribromide (that is, bromine in *N*-potassium bromide) of molecular concentration a be P . Then, in the solution under discussion, the colour is due partly to free bromine (say, concentration x) and partly to

* The formation of Br_3^- ions would be attended by diminution of conductivity owing to their probably having lower mobility. Bray and Mackay (*J. Amer. Chem. Soc.*, 1910, **32**, 919) have shown the diminution in conductivity brought about by dissolving iodine in aqueous potassium iodide, and caused by the lower mobility of the I_3^- ion.

potassium tribromide ($a-x$). Now, assuming that decrease in colour is proportional to the amount of potassium tribromide formed, then the colour of a solution of a gram-mol Br

when conc. of free Br is 0 is P

” ” ” ” x ” C

” ” ” ” a (that is, Br_2Aq) is a ,

so that proportionally

$$\frac{a}{x} = \frac{a-P}{c-P} \text{ or } x = \frac{a(c-P)}{a-P}.$$

The concentration of the free bromine being thus found, that of the potassium tribromide is $a-x$. This, subtracted from the total potassium bromide concentration, gives the uncombined potassium bromide. From these the dissociation constant in the equation:

$$k(\text{KBr}_3) = \text{Br}_2 \times (\text{KBr})$$

can then be calculated.

The value of k is shown for the experiments of table II. The numbers in the first three columns are taken from table II. Those in the fourth are taken from the N -potassium bromide curve in Fig. 2.

TABLE III.

Dissociation Constant of Potassium Tribromide.

Total concentration, KBr.	Total Br = a .	Colour = C .	Colour of KBr_3 solution of concentration $a = P$.	Free Br = x .	KBr_3 = $a - x$.	Free KBr = total KBr - ($a - x$).	k .
0.1	0.0255	0.015	0.0078	0.0104	0.0151	0.0849	0.058
0.1	0.0305	0.018	0.0095	0.0123	0.0182	0.0818	0.055
0.1	0.0620	0.040	0.0198	0.0297	0.0323	0.0667	0.059
0.1	0.0712	0.0485	0.0226	0.0379	0.0333	0.0667	0.076 (?)
0.1	0.1071	0.075	0.0372	0.0579	0.0492	0.0508	0.060
0.4	0.0665	0.027	0.0212	0.0085	0.0580	0.3420	0.050
0.4	0.0708	0.029	0.0225	0.0095	0.0613	0.3687	0.057
0.4	0.0984	0.041	0.0332	0.0115	0.0869	0.3131	0.041
0.4	0.1239	0.053	0.0431	0.0152	0.1087	0.2913	0.041
0.4	0.1305	0.056	0.0458	0.0157	0.1148	0.2852	0.040
0.4	0.1835	0.0785	0.0628	0.0239	0.1596	0.2404	0.036

In taking the colour of the potassium tribromide solutions from Fig. 2, the smoothed curve has not been used, but each pair of consecutive points has been joined by straight lines. The values of k obtained in this way are of the same order of magnitude and constancy as those obtained by Worley, the variations being from 0.03 to 0.07.

A large number of determinations were made to see whether

sodium and hydrogen bromides behaved in the same way, and from the examples given in the next tables it will be seen that the results are quite similar.

TABLE IV.

Dissociation Constant of Sodium Tribromide.

Concen- tration, NaBr.	Total Br = a .	Colour = C .	Colour of NaBr ₃ solution of concen- tration $a = P$.	Free Br = x .	NaBr ₃ $= a - x$.	Free NaBr = total NaBr - $a - x$.	k .
0.1	0.0519	0.036	0.020	0.0260	0.0259	0.0741	0.074
0.1	0.0689	0.046	0.0255	0.0327	0.0362	0.0638	0.065
0.1	0.0805	0.055	0.0295	0.0402	0.0403	0.0597	0.060
0.1	0.1110	0.077	0.040	0.0580	0.0530	0.0470	0.052
0.4	0.0427	0.019	0.0165	0.0041	0.0386	0.3614	0.038
0.4	0.0762	0.032	0.028	0.0063	0.0699	0.3301	0.030
0.4	0.0866	0.0368	0.0315	0.0083	0.0783	0.3207	0.034
0.4	0.1214	0.053	0.0425	0.0161	0.1053	0.2947	0.045
0.4	0.1720	0.077	0.060	0.0261	0.1459	0.2541	0.045
1.0	0.0323	0.013	—	—	—	—	—
1.0	0.0647	0.024	—	—	—	—	—
1.0	0.1037	0.0375	—	—	—	—	—
1.0	0.1415	0.049	—	—	—	—	—
1.0	0.1824	0.0635	—	—	—	—	—
1.0	0.2440	0.076	—	—	—	—	—

TABLE V.

Dissociation Constant of Hydrogen Tribromide.

Concen- tration, HBr.	Total Br = a .	Colour = C .	Colour of HBr ₃ solution of concen- tration $a = P$.	Free Br = x .	HBr ₃ $= a - x$.	Free HBr = total HBr - $(a - x)$.	k .
0.1	0.060	0.039	0.020	0.0285	0.0315	0.0685	0.062
0.1	0.090	0.062	0.031	0.0473	0.0427	0.0573	0.064
0.4	0.065	0.027	0.022	0.0098	0.0552	0.3448	0.061
0.4	0.133	0.0585	0.046	0.0191	0.1139	0.2861	0.048
1.0	0.042	0.015	—	—	—	—	—
1.0	0.079	0.027	—	—	—	—	—
1.0	0.107	0.037	—	—	—	—	—
1.0	0.149	0.052	—	—	—	—	—
1.0	0.188	0.0635	—	—	—	—	—

If curves exhibiting the relation between bromine concentration and colour are plotted, they are found to be almost coincident with the corresponding ones for potassium bromide, the values for k being likewise practically the same.

Summary.

1. Bromides lighten the colour of aqueous bromine solution, the diminution depending on the amount of bromide added. The

results obtained with sodium, potassium, and hydrogen bromides are similar.

2. After the concentration of the bromide has reached normal, further addition produces little effect on the colour. It is therefore assumed that in such solutions practically the whole of the bromine is in the combined state.

3. In bromide solutions of concentration less than normal, the colour is due partly to free and partly to combined bromine, the amounts of which can be calculated with the aid of the curves.

4. Application of the law of mass-action to the results supports the view that the principal reaction causing the colour change is the formation of a tribromide, the dissociation constant of which is about 0.05.

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