

A Spectrophotometric Study on Complex Formation in Dilute Aqueous Solution of Cupric Bromide

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Cupric bromide in aqueous solution exhibits an absorption band at 281 $m\mu$, at which wavelength cupric and bromide ions display practically no absorption. This can obviously be explained only by means of complex formation between cupric and bromide ions. Quantitative study proves difficult, however, because of the low degree of complex formation and of its complicated nature¹.

In sufficiently dilute solution, however, the complex $\text{Cu}(\text{H}_2\text{O})_3\text{Br}^+$ must be practically the only one. The application of the law of mass action to such a solution gives

$$[\text{Cu}^{++}] [\text{Br}^-] / [\text{CuBr}^+] = K = K_0/F \quad (1)$$

where

$$f_{\text{Cu}^{++}} f_{\text{Br}^-} / f_{\text{CuBr}^+} = F \quad (2)$$

is the activity coefficient and K_0 is the thermodynamic dissociation constant. The extinction of a 1 cm layer of such a solution is, according to Beer's law

$$e = \epsilon [\text{CuBr}^+] \quad (3)$$

where ϵ is the molar extinction coefficient. From (1) and (3) we obtain

$$\log \frac{e}{(c - e/\epsilon)(2c - e/\epsilon)} = \log \epsilon / K_0 - pF \quad (4)$$

where c denotes the molarity of the cupric bromide solution. The activity coefficient may be represented by the Debye-Hückel equation

$$pF = \frac{2.04 \sqrt{I}}{1 + \alpha \sqrt{I}} - BI \quad (5)$$

In sufficiently dilute solution e/ϵ in equation (4) is negligibly small in comparison with c and $2c$. In such a case equations (4) and (5) can be used for the calculation of the quantities ϵ/K_0 , α and B from the extinctions of a series of cupric bromide solutions, where the ionic strength is varied by addition of lithium or sodium perchlorate or perchloric acid². In practice the magnitude of the molar extinction coefficient determines how dilute the cupric bromide solutions may be.

Table 1. Light absorption measurements in dilute cupric bromide solutions with perchloric acid additions at 25° C.

\sqrt{I}	$c_{\text{Cu}} \cdot 10^3$	e ($\lambda = 280 \text{ m}\mu$)	$\log \frac{e}{(c-e/\epsilon)(2c-e/\epsilon)}$
0.110	3.99	0.0274	2.938
0.151	7.62	0.0860	2.875
0.205	13.97	0.250	2.814
0.291	19.35	0.395	2.731
0.352	19.35	0.358	2.688
0.524	25.80	0.518	2.599
0.687	25.80	0.472	2.558
0.826	23.93	0.402	2.553
1.136	23.93	0.430	2.583
1.424	19.35	0.356	2.685
1.640	19.35	0.472	2.810
1.893	14.78	0.452	3.028

In Table 1 the measurements in perchloric acid solutions are recorded. Similar measurements were carried out in lithium and sodium perchlorate solutions. Wavelengths of 270, 280, 290, 300 and 310 $\text{m}\mu$ were used. The results were independent of wavelength. For the constants α and B the following values were obtained:

	α	B
HClO_4	1.476	0.252
LiClO_4	1.476	0.213
NaClO_4	1.476	0.190

In the calculation the value $\epsilon = 1480$, obtained in a way described later in this paper, was used. These results did not, however, differ much from the results calculated using the value $\epsilon = \infty$. For instance in perchloric acid solution the values $\alpha = 1.472$ and $B = 0.250$ were obtained when the value $\epsilon = \infty$ was used. The values of α and B are of a reasonable magnitude. This is thus in agreement with the assumption made above that in the dilute cupric

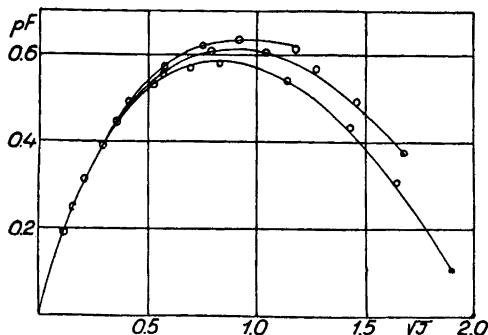


Fig. 1. Activity coefficient of the first cupric bromide complex in perchloric acid (lower curve), in lithium perchlorate (middle curve) and in sodium perchlorate (upper curve) solutions.

bromide solutions investigated, the first complex $\text{Cu}(\text{H}_2\text{O})_3\text{Br}^+$ is practically the only one present. Supposing that the complex in question is a higher one we obtain from the experimental data an unreasonably steep curve representing the relation between pF and \sqrt{I} . In Fig. 1 the activity coefficient is plotted against the ionic strength.

For the quotient ϵ/K_0 the value 1340 was obtained by the above way. A more accurate value for this quantity can, however, be obtained by means of measurements in cupric bromide — sodium bromide solutions. In this case the equation

$$\log \frac{e}{(c_{\text{Cu}} - e/\epsilon)(c_{\text{Br}} - e/\epsilon)} = \log \epsilon/K_0 - pF \quad (6)$$

was used where c_{Cu} is the total copper and c_{Br} the total bromide concentration. This equation is analogous to equation (4) and the lower the bromide concentration the better is its validity. In Table 2 a series of experiments in cupric bromide — sodium bromide solutions is recorded. These experiments were also carried out at 280 $m\mu$. It is significant that the value of ϵ/K_0 calculated by means of equation (6) proved to be nearly independent of the value of ϵ used. On the contrary α , and even more B , are highly dependent on the value of ϵ . For instance the following values were obtained:

ϵ	$\log \epsilon/K_0$
∞	3.1183
1420	3.1202
1000	3.1206

By means of this extrapolation procedure the value of ϵ/K_0 may thus be determined irrespective of the unquestionable existence of higher complexes.

Finally the thermodynamic dissociation constant K_0 may be estimated from the data recorded in Table 2 by means of the equation

$$K_0 = \frac{e/c_{\text{Cu}}}{\epsilon/K_0 - e/c_{\text{Cu}} [\text{Br}^-] F} \quad (7)$$

Table 2. Light absorption of mixed solutions of cupric bromide and sodium bromide. The estimation of the thermodynamic dissociation constant of the complex $\text{Cu}(\text{H}_2\text{O}_3)\text{Br}^+$.

\sqrt{I}	e	$c_{\text{Cu}} \cdot 10^3$	c_{Br}	pF	K_0	
					$(\epsilon = \infty)$	$(\epsilon = 1480)$
0.109	0.027	3.99	0.00798	0.190	6.76	0.95
0.205	0.247	13.97	0.0279	0.313	1.77	1.10
0.348	0.112	2.17	0.1143	0.446	0.80	0.73
0.410	0.825	13.97	0.1440	0.489	1.18	1.05
0.572	0.860	8.38	0.309	0.570	1.30	1.21
0.598	0.153	1.343	0.353	0.580	1.26	1.18
0.640	0.154	1.236	0.405	0.593	1.17	1.10
0.850	0.159	0.820	0.720	0.631	1.19	1.15
0.941	0.153	0.671	0.883	0.635	1.11	1.08
					mean value	1.06

which follows from equation (1). This equation is strictly valid only at a sufficiently low bromide concentration, but by means of an extrapolation procedure the value of K_0 can obviously be estimated. The calculation was carried out as follows. At first the activity coefficient in sodium perchlorate solutions was calculated by means of equation (4) using the value $\epsilon = \infty$. Then the value of ϵ/K_0 was estimated by means of equation (6) using the value $\epsilon = \infty$. Using these values of F and ϵ/K_0 the thermodynamic constant K_0 was now calculated by means of equation (7). These values are recorded in Table 2. As is seen these K_0 values are within the limits of experimental error independent of the bromide concentration except at low concentrations. With the aid of the mean value of these approximate K_0 values the molar extinction coefficient ϵ can now be calculated. With this ϵ value the calculation process was repeated and after a short series of approximations the values of the constants did not vary. The final values of K_0 are represented in the last column of Table 2. The mean value of K_0 was $K_0 = 1.06$ and the corresponding value of the molar extinction coefficient was $\epsilon = 1480$ ($\lambda = 280 \text{ m}\mu$).

It is interesting that the K_0 values obtained at $280 \text{ m}\mu$ are not dependent on the bromide concentration. This is not due to the absence of higher complexes because at other wavelengths, for instance at $310 \text{ m}\mu$, the K_0 values obtained in the above way are highly dependent on the bromide concentration. The explanation is no doubt as follows. When the higher mononuclear complexes are considered, the equation

$$K_0 = \frac{e/c_{\text{Cu}}}{\varepsilon/K_0 - e/c_{\text{Cu}} [\text{Br}^-] F + \frac{1}{F [\text{Br}^-]} \sum \varepsilon_{\nu} [\text{Br}^-]^{\nu} / K_{\nu} - \frac{e}{c_{\text{Cu}} [\text{Br}^-] F} \sum [\text{Br}^-]^{\nu} / K_{\nu}} \quad (8)$$

is obtained instead of equation (7). In this equation K_{ν} denotes the dissociation constant of the complex CuBr_{ν} , and is defined by

$$K_{\nu} = \frac{[\text{Cu}^{++}] [\text{Br}^{-\nu}]}{[\text{CuBr}_{\nu}]} \quad (9)$$

ε_{ν} being the corresponding molar extinction coefficient. In the sums only terms with $\nu \geq 2$ are included. Equation (8) differs from equation (7) by two additional sum terms of which the first one is positive and contains molar extinction coefficients and is therefore dependent on the wavelength. The second one is negative. It is therefore possible that at a certain wavelength and in a limited range of bromide concentration the higher complexes have no effect on the results within the limits of the experimental error.

A Beckman Quartz Spectrophotometer Model DU with 1 cm and 5 cm cells was used in the light absorption measurements. The chemicals when not of the best quality obtainable, were recrystallized many times. Concerning further experimental details, the reader is referred to the previous papers by the present author^{2,3}.

SUMMARY

Complex formation in concentrated solutions of cupric bromide is very complicated but in sufficiently dilute solutions the complex $\text{Cu}(\text{H}_2\text{O})_3\text{Br}^+$, obviously, is practically the only one. Complex formation in such dilute solutions is so slight that the concentration of the complex ion can be neglected as compared to the total copper concentration but the molar extinction coefficient is so large that it is possible to follow the change in the concentration of the complex. Therefore the determination of the activity coefficient of the complex in alkali perchlorate and perchloric acid solutions was possible spectrophotometrically and the accuracy obtained was considerable. Further a method for the estimation of the thermodynamic dissociation constant from extinction measurements is described and it is applied to dilute aqueous solutions of cupric bromide.

REFERENCES

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