of pyridine which was reported[16] has since been shown[17] to be in error.

Acknowledgment.—This work was supported by a grant from the Office of Ordnance Research (Army Research Office) for which we wish to express our gratitude.

(16) H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **75**, 3865 (1953).

(17) N. Muller and W. J. Wallace, *J. Org. Chem.*, **24**, 1151 (1959).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
OREGON STATE COLLEGE, CORVALLIS, OREGON

Bromide Complexes of Thallium(I)[1]

BY ALLEN B. SCOTT, ROLAND G. DARTAU, AND SURANG SAPSOONTHORN

Received July 21, 1961

The solubility of TlBr in KBr solutions, and the absorption spectra of solutions containing both TlBr and KBr, have been analyzed. The data are consistent with the assumed existence of the complexes TlBr, $TlBr_2^-$, and $TlBr_4^{---}$, whose dissociation constants and molar absorptivities are given.

Introduction

Thallium(I) has been found to form chloride complexes having the formulas TlCl and $TlCl_2^-$, and some evidence has been reported for the existence of higher complexes in aqueous solutions of high chloride concentration.[2-4] Nilsson[4] also reported experiments which show that thallium(I) forms complexes of the type $TlX_q^{-(q-1)}$ with bromide and iodide, q ranging from one through four, and determined formation constants (expressed in concentration units) at an ionic strength of 4 M, in NaBr–$NaClO_4$ mixed solutions. However, even though the ionic strength was kept constant, activity coefficients in such solutions may be expected to vary widely as the NaBr/$NaClO_4$ ratio varies. Robinson[5] reported for 4 m NaBr, $\gamma = 0.939$; Jones[6] reported for 4 m $NaClO_4$, $\gamma = 0.627$. Constants such as Nilsson's $k_3 = [TlBr_4^{-3}]/[Br^-]^3$, where [ ] represents concentration, may vary by a factor of two or more over the range of compositions used. It is of course uncertain what activity coefficients should be used for multiply charged ions in this case. We conclude that the formulas of complexes reported by Nilsson are not established.

We have determined the solubility of TlBr in solutions of varying KBr concentration and have calculated dissociation constants for the complexes as was done for the chloride complexes by Hu and Scott.[2] The use of KBr solutions, whose activity coefficients are known, rather than a mixture of two salts, makes it possible to determine dissociation constants for TlBr and $TlBr_2^-$ involving activities rather than concentrations. Further, since the mean ionic activity coefficient of KBr is fairly constant in the range 1–4 m, lying in the range 0.589–0.612, it is likely that concentration constants for higher complexes will remain fairly constant with varying KBr concentration. This is not true of NaBr, for γ varies[6] from 0.690 at 1 m to 0.939 at 4 m. We then have utilized these constants in the analysis of the absorption spectra of solutions of TlBr in KBr, as a means both of testing the dissociation constants and determining the molar absorptivities of the several species, using the method of Scott and Hu.[3]

Experimental

Solutions of KBr were saturated with TlBr at 25°; the solutions were analyzed for thallium(I) polarographically by reduction at the dropping mercury cathode.[7] At each concentration of KBr not less than four analyses were performed: one of a solution brought to equilibrium from oversaturation by three days agitation, one of a solution

---

(1) Presented before the Northwest Regional Meeting, the American Chemical Society, Richland, Washington, June 16, 1960. Taken from the M.S. theses of Roland G. Dartau (1958) and Surang Sapsoonthorn (1960), Oregon State College. Research Paper No. 419, O.S.C. Monographs.

(2) K. H. Hu and A. B. Scott, *J. Am. Chem. Soc.*, **77**, 1380 (1955).

(3) A. B. Scott and K. H. Hu, *J. Chem. Phys.*, **23**, 1830 (1955). In this paper, Table II, column headings should read $\epsilon_{w,x,y} \times 10^{-3}$.

(4) R. O. Nilsson, *Arkiv Kemi*, **10**, 363 (1957).

(5) R. A. Robinson, *Trans. Faraday Soc.*, **35**, 1217 (1939).

(6) J. H. Jones, *J. Phys. Chem.*, **51**, 516 (1947).

(7) Y. Terui, *Bull. Inst. Phys. Chem. Research* (Tokyo), **17**, 595 (1938).

similarly brought from undersaturation, and an additional one of each of the solutions after standing another day. At each KBr concentration the four analyses, and any replicates, agreed within the estimated error of the polarographic method, the relative standard deviation for analyses at each concentration averaging 1%.

Curves of polarographic wave height *vs.* thallium concentration at each of the KBr concentrations used were determined using solutions of known thallium concentration; the solubility then was found by a short extrapolation. The KBr served as the supporting electrolyte; maxima were suppressed by the addition of methyl red.

Absorption spectra were measured by means of a Beckman spectrophotometer, Model DU, using distilled water as the reference.

Results

Solubility results are presented in Fig. 1. As previously discussed,[2,8] a plot of the quantity (solubility − $[Tl^+]$) *vs.* $[Br^-]$ should give a straight line of intercept [TlBr] and slope $[TlBr]/K_2$, where the brackets represent concentration in mole/liter, and K_2 is defined below, provided the only complexes are TlBr and $TlBr_2^-$. Such a plot, shown as curve B of Fig. 1, is nearly linear at low Br^- concentration, but by its pronounced upward curvature at high Br^- concentration demonstrates the existence of one or more complexes of $q > 2$. Tl^+ concentration was calculated from the solubility product of TlBr, 3.83×10^{-6} mole²/l.², reported by Terui.[7]

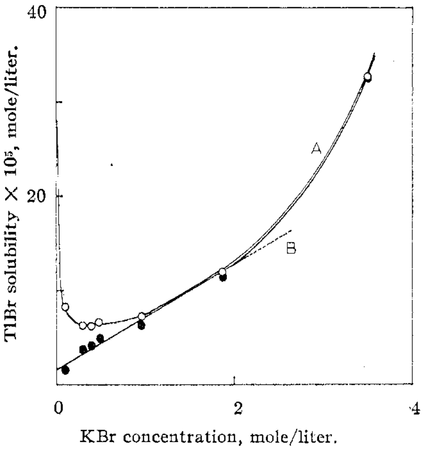

Fig. 1.—Solubility, *S*, of TlBr in KBr solutions (curve A); B, $S - [Tl^+]$.

From the intercept and the slope at low Br^- concentration, these constants were evaluated

$$TlBr_{(solid)} = TlBr_{(soln)};\quad [TlBr] = 1.6 \times 10^{-5}\ \text{mole/l.}$$

$$TlBr_{(soln)} = Tl^+ + Br^-;$$

$$K_1 = \frac{[Tl^+][Br^-]f_\pm^2}{[TlBr]} = 0.24\ \text{mole/l.}$$

$$TlBr_2^- = TlBr + Br^-;$$

$$K_2 = \frac{[TlBr][Br^-]}{[TlBr_2^-]} = 0.30\ \text{mole/l.}$$

The mean activity coefficient $f_\pm$ was taken to be that of the KBr itself, as given by Harned[9] but corrected for use with volume concentrations. Since the concentration of a singly charged ion enters in both numerator and denominator of K_2 it is, to a first approximation, a thermodynamically correct constant, as is K_1. The activity coefficient of TlBr is assumed to be unity.

The solubility data are inconsistent with the assumed existence of $TlBr_3^{--}$, as an upward deviation from linearity of curve B, Fig. 1, would be apparent at concentrations as low as 1 *M* KBr were the curve also to pass through the observed solubility at 3.50 *M* KBr.

We may write for the dissociation: $TlBr_4^{---} = TlBr_2^- + 2Br^-$

$$K_{4c} = \frac{[TlBr_2^-][Br^-]^2}{[TlBr_4^{---}]}$$

From the excess solubility (over that calculated on the basis of $TlBr_2^-$ and TlBr as the only complexes) in 3.50 *M* KBr, K_{4c} was found to be 16. Since this is a constant involving concentrations rather than activities, it is strictly valid only in 3.50 *M* KBr; however, as previously pointed out, it may be expected to hold with fair accuracy at lower concentrations. The absorption measurements bear out this expectation.

The foregoing constants were used to analyze the absorption spectra of KBr solutions containing added TlBr. These spectra have a pronounced maximum in absorption near 260 mμ, the peak height and location varying with both Br^- and total Tl(I) concentration. Solutions were prepared having the KBr concentrations 0.96, 1.87, 2.72, and 3.50 mole/l. Concentrations of TlBr in each of these KBr solutions ranged from zero to nearly the solubility at each KBr concentration. Examples of the absorption spectra are shown in Fig. 2. Letting *t*, *v*, *w*, *x*, *y*, and *z* represent the concentrations, in mole/liter, of total Tl(I), $TlBr_4^{---}$, $TlBr_2^{--}$, Tl^+, TlBr, and Br^-, respectively, we have, from the definitions of the constants

$$t = v + w + x + y = w\frac{z^2}{K_{4c}} + 1 + \frac{K_1K_2}{zf_\pm^2} + \frac{K_2}{z}$$

At any *z* and *t*, *w* thus is readily calculable.

---

[8] C. A. Reynolds and W. J. Argersinger, *J. Phys. Chem.*, **46**, 417 (1952)

[9] H. S. Harned, *J. Am. Chem. Soc.*, **51**, 416 (1929).

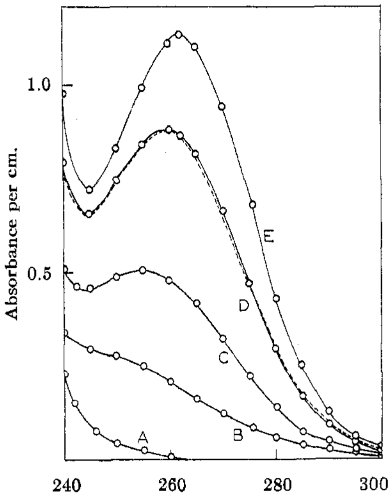

Fig. 2.—Absorption spectra of mixed TlBr–KBr solutions. Concentration TlBr × 10^5 – concentration KBr, M: A, 142.3 – 0.0; B, 6.70 – 0.96; C, 11.80 – 1.87; D, 18.25 – 2.72 (broken curve calculated from molar absorptivities, Fig. 4); E, 21.15 – 3.50.

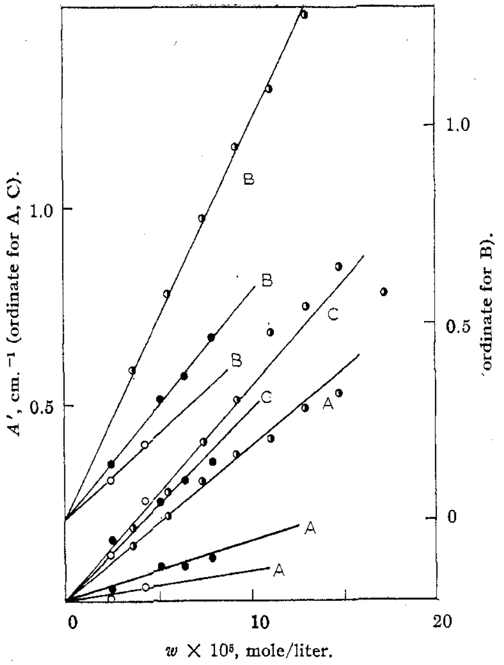

Fig. 3.—Net absorbance per cm., A', as a function of $TlBr_2^-$ concentration, w. Br^- concentration: ○, 0.96; ●, 1.87; ◑, 3.50 M. Curves A, 280 mμ; B, 260 mμ; C, 240 mμ. Slopes for 0.96 and 3.50 M KBr are the same at 240 mμ.

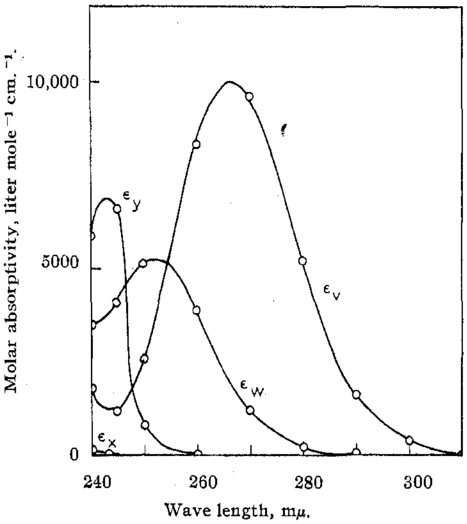

Fig. 4.—Molar absorptivities of TlBr (ϵ_y), $TlBr_2^-$ (ϵ_w), $TlBr_4^{---}$ (ϵ_v), and Tl^+ (ϵ_x).

The absorbance per cm., A/b, is

$$A/b = v\epsilon_v + w\epsilon_w + x\epsilon_x + y\epsilon_y + z\epsilon_z$$

where the ϵ's are the molar absorptivities of the species indicated by the subscripts. ϵ_x may be found directly from absorption measurements in solutions of TlBr with no added Br^- (in which association is negligible), an example of which is displayed in curve A, Fig. 2. $x\epsilon_x$ was never greater than 0.001 in the solutions studied here, and was neglected. $z\epsilon_z$ was significant at 240 and 245 mμ. ϵ_z was found from the slope of a plot of A/b of KBr solutions against concentration. The values used were 0.085 l. mole^{-1} cm.$^{-1}$ at 240 mμ and 0.021 at 245 mμ. At greater wave lengths the absorbance of KBr was very small and appeared to be independent of concentration; we presume it to be due chiefly to accidental contamination. At each wave length the absorbance per cm. of all KBr solutions was averaged, and the result taken as $z\epsilon_z$ at that wave length. To correct further, A/b was taken as zero at 320 mμ, and all measurements at smaller wave lengths taken relative to the value at 320 mμ. Then we have

$$A/b - z\epsilon_z = w\frac{z^2}{K_{4c}}\epsilon_v + \epsilon_w + \frac{k^2}{z}\epsilon_y = A'$$

The net absorbance per cm., A', was plotted against w at z = 0.96, 1.87, and 3.50 M, for a series of wave lengths from 240 to 300 mμ. The curves for 240, 260, and 280 mμ are shown for illustration in Fig. 3. The curves were generally linear. From the three slopes, corresponding to each of the three values of z, the ϵ's may be obtained. These are presented in Fig. 4. Due to the overlap of the absorption bands of TlBr, $TlBr_2^-$, and $TlBr_4^{---}$, the results are not considered as accurate as those previously obtained for the chloride complexes[3]; also, here the high absorbance of Br^- itself at 240 mμ renders the absorption curve steep in this region, with a large resultant probable error.

The molar absorptivities thus obtained, as well as the constants given by the solubility data, were tested by computing the absorption curve of 2.72 M KBr in which the concentration of TlBr was 18.25×10^{-5}. This is shown by the broken curve D of Fig. 2. Agreement with the observed (solid) curve is satisfactory, which confirms our contention that use of K_{4c} is justified at KBr concentrations less than 3.50 M.

While it must be agreed that the assignment of formulas and stability constants for complexes are in this and similar cases simply an attempt to fit an experimental curve with an equation in the form of a power-series, we conclude that the assumption of the existence of TlBr, $TlBr_2^-$, and $TlBr_4^{---}$ is adequate to account for the results of solubility and optical absorption experiments.

Acknowledgment.—We wish to acknowledge the assistance of Professor H. Freund and Mr. C. R. Schneider in making the polarographic measurements.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF KANSAS, LAWRENCE, KANSAS

Electrochemical and Infrared Evaluation of the Formation Constants of Aquo–Copper(II) Complexes in Nitromethane

BY ROBERT C. LARSON AND REYNOLD T. IWAMOTO

Received September 29, 1961

The individual formation constants for aquo–copper(II) complexes in nitromethane have been evaluated by electrochemical and spectrophotometric methods. These values have been compared with those calculated for aquo–copper(II) complexes in ethanol from previously published data. Average log k values in nitromethane are 2.90, 1.92, 1.22, 0.94, 0.52, and ~0.50. Log k values in ethanol are −0.23, −0.51, −0.86, −0.93, −1.14, and −1.17.

During the last decade there has been a growing interest in the use of non-aqueous solvents to obtain information fundamental to better understanding the nature of ion–solvent interactions. Surprisingly, the effect of residual water on the behavior of ions in non-aqueous media, however, has received very little careful systematic consideration—not as much as it deserves. The fact that even solvents of 99.98% purity, *i.e.*, 0.02% in water, are still *ca.* 0.01 M in water, a value of the same order of magnitude as the limited solubility of inorganic substances in non-aqueous solvents, makes it imperative that this problem is examined carefully before many more studies in this area are undertaken.

Jørgensen[1] and Minc and Libuś[2] have examined the formation of aquo–copper(II) ions, among other transition group metals, in ethanol and have derived some quantitative information on the selectivity of solvation by water molecules. An average formation constant, $(k_1 k_2 k_3 \ldots k_6)^{1/6}$, of $10^{-0.73}$ has been reported by Jørgensen. Individual aquo–copper(II) formation constants in ethanol have been evaluated from the data of Minc and Libuś by a $\bar{n}$ *vs.* $-\log [H_2O]$ plot. An "average" formation constant of $10^{-0.81}$ has been computed from the individual k's.

In a preliminary study[3] of solvent effects on the polarographic behavior of copper(II) ion, two well separated waves of equal height were observed in nitromethane with these $E_{1/2}$ values

$$E_{1/2\,\mathrm{Cu(II),Cu(I)}} \quad > +0.8 \text{ v. } vs. \text{ s.c.e.}$$

$$E_{1/2\,\mathrm{Cu(I),Cu(Hg)}} \quad +0.21 \text{ v. } vs. \text{ s.c.e.}$$

The large positive shift of the Cu(II),Cu(I) half-wave potential in nitromethane from that for the same couple in water ($E^0_{\mathrm{Cu(II),Cu(I)}} = -0.09$ v. *vs.* s.c.e.) is due to the lower solvation energy of Cu(II) ion in nitromethane. The Cu(II),Cu(I) half-wave potential, as might be expected, shifts markedly to more negative values on the addition of water. This marked shift is caused by an increase in the solvation energy of copper(II) ion as a result of selective solvation by water molecules.

---

(1) C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 175 (1954).

(2) S. Minc and W. Libuś, *Roczniki Chem.*, **29**, 1073 (1955).

(3) I. V. Nelson, R. C. Larson, and R. T. Iwamoto, *J. Inorg. & Nuclear Chem.*, to be published.