low as 30 kbars,[9,10] and consequently at this pressure the polymer is stable relative to the monomer; that is, the pressure is above the polymerization pressure[11] for the monomer–polymer equilibrium. The volume of polymerization of carbon disulfide at 1 bar is about $-20 \text{ cm}^3 \text{ mol}^{-1}$ according to the reported densities of the polymer.[9,12] In the range 0–30,000 kg cm^{-2} carbon disulfide compresses[11,13] over 20 cm^3 mol^{-1}, most of which occurs[13] in the first 5000 kg cm^{-2}, and the compressibility of the polymer is undoubtedly much less. If it is assumed that the volume of polymerization averages $-10 \text{ cm}^3 \text{ mol}^{-1}$ in the range 0–30 kbars, which seems an upper limit to the decrease, then the polymer is not more than 7 kcal mol^{-1} of Gibbs energy unstable relative to the monomer of 1 atm. The difference in volume between the elements and the polymer is small,[9,12] so the pressure should have little effect on the Gibbs energy change between the elements and the polymer. It follows from this that the polymer must be unstable relative to the elements by well over 15 kcal mol^{-1} in the Gibbs energy over a wide pressure range. The failure of carbon and sulfur to react to give the polymer is therefore not unexpected.

Somewhat similar arguments apply to carbon diselenide. As carbon diselenide is less stable relative to the elements than carbon disulfide,[8] it is even less likely that the reaction of carbon and selenium will yield the polymer. Carbon ditelluride will be even less stable relative to the elements, and this is probably a partial explanation of why it has never been prepared. In addition, it should polymerize readily.

The polymerization of carbon disulfide is irreversible in the sense that once the polymer is formed it is not reported to depolymerize. In principle, the monomer–polymer equilibrium is undoubtedly mobile. It appears that an appreciable rate is obtained only well above the polymerization pressure.

(9) E. G. Butcher, M. Alsop, J. A. Weston, and H. A. Gebbie, *Nature*, **199**, 756 (1963).

(10) L. A. Wall and D. W. Brown (*J. Polymer Sci.*, **4**, 1151 (1964)) have reported obtaining small yields of a black substance by irradiating carbon disulfide with up to 400 Mrads of Co^{60} radiation at pressures up to 15 kbars. Unfortunately, the material was not identified as poly(carbon disulfide), and there are too many uncertainties at present for the observations to be considered relevant to the thermodynamics of polymerization of carbon disulfide.

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(12) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **74**, 399 (1942).

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Bismuth Iodide Complexes in Aqueous Solution of High Iodide Concentration

BY G. P. HAIGHT, JR., AND L. JOHANSSON

The bismuth iodide system has been investigated earlier using potentiometric and solubility measurements by Ahrland and Grenthe.[1] They established a maximum coordination number $N = 6$ for $[\text{I}^-] \leq 0.5 M$. Eve and Hume[2] studied the system spectrophotometrically and found, at $0.4 M \leq [\text{I}^-] \leq 1.4 M$, a change in the ultraviolet and visible spectra, which they attributed to the partial formation of BiI$_7^{4-}$.

Dyrssen[3] has performed a study of the solubility of BiI$_3$ and BiOI and suggests that Bi$_2$I$_9^{3-}$ is formed besides the mononuclear complexes. The arguments for Bi$_2$I$_9^{3-}$ are not very strong, however,[4] and this complex is probably only formed (if at all) at bismuth concentrations higher than those employed in this study and in that of Eve and Hume.[2]

Recent studies[5] have indicated the formation of BiBr$_8^{5-}$ in solutions of bismuth bromide in HBr[5e] and of SnI$_6^{6-}$ in tin(II) iodide[5g] systems, in both cases without the intermediate formation of any MX$_7^{n-7}$ complex. This prompted us to consider the possibility that the results of Eve and Hume could be interpreted as a formation of BiI$_8^{5-}$ instead of BiI$_7^{4-}$.

Our primary aim was, however, to investigate the usefulness of a new kind of solubility technique on this system. Previously, we have used salts with three different ions to study various complex systems,[5] *e.g.*, [(CH$_3$)$_4$N]$_2$SnI$_4$(s) on the tin(II) iodide system.[5g] It was then noted that if the solutions were simultaneously saturated also with the ligand salt of the third ion, the results would be particularly easy to interpret.

For the bismuth iodide system, Co(NH$_3$)$_6$BiI$_6$(s) was chosen as the three-ion salt.[6] The second salt, Co(NH$_3$)$_6$I$_3$(s), has a very low solubility at high $[\text{I}^-]$. Therefore, at high $[\text{I}^-]$, Co(NH$_3$)$_6$BiI$_6$(s) is partly converted to Co(NH$_3$)$_6$I$_3$(s) and solutions become saturated with both salts. This establishes the equilibrium

$$\text{Co(NH}_3)_6\text{BiI}_6 + n\text{I}^- \rightleftharpoons \text{Co(NH}_3)_6\text{I}_3 + \text{BiI}_{3+n}{}^{n-} \quad \text{(I)}$$
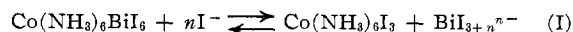
The method works even if the solubility of the second salt is higher than that of the first one, provided enough of the second salt is added initially. It will be shown below that the mixture acts, in part, as if BiI$_3$(s) were present alone. We shall designate [Bi(III)] as the "solubility" of the solid phase. Thus, the slope of a logarithmic plot of the solubility (the total bismuth concentration) *vs.* $[\text{I}^-]$ is simply $\bar{n} - 3$. However, for any $[\text{I}^-]$ the solubility over the mixture is necessarily lower than that of BiI$_3$(s); otherwise the double salt would not be formed. While the actual solubility of BiI$_3$(s) is far too high[1] at $[\text{I}^-] \geq 1 M$, the solubility over the mixture is low enough for convenient mea-

(1) S. Ahrland and I. Grenthe, *Acta Chem. Scand.*, **11**, 1111 (1957).

(2) A. J. Eve and D. N. Hume, *Inorg. Chem.*, **6**, 331 (1967).

(3) D. Dyrssen and A. C. Yen, "Solvent Extraction Chemistry," North-Holland Publishing Co., Amsterdam, 1967, p 470.

(4) D. Dyrssen, private communication. The average number of ligands per bismuth ion (ref 3, p 473) should be 7.5 rather than 4.5, if the contribution from the solubility to [I$^-$]$_{tot}$ is taken into account.

(5) (a) G. P. Haight, Jr., *Acta Chem. Scand.*, **16**, 209 (1962); (b) G. P; Haight, Jr., J. Zoltewicz, and W. Evans, *ibid.*, **16**, 311 (1962); (c) G. P. Haight, Jr., C. H. Springer, and O. J. Heilmann, *Inorg. Chem.*, **3**, 195 (1964). (d) G. P. Haight, Jr., and B. Y. Ellis, *ibid.*, **4**, 249 (1965); (e) G. P. Haight, Jr., and J. Preer, *ibid.*, **5**, 656 (1966); (f) G. P. Haight, Jr., and L. Nilsson, *Acta Chem. Scand.*, **20**, 486 (1966); (g) G. P. Haight, Jr., and L. Johansson, *ibid.*, in press.

(6) F. Ephraim and P. Mosimann, *Ber.*, **54**, 396 (1921).

surement up to $[I^-] = 4\ M$. One can say, generally, that the two-salt method makes possible an extension of solubility measurements to higher ligand concentrations. Important from a practical point of view is the fact that the exact composition of the three-ion salt need not necessarily be known. That is, if the formula is written $x[Co(NH_3)_6I_3] \cdot BiI_3(s)$, x does not enter in any equations. Even if x changes for some ligand concentration, the solubility would not be affected, provided only that $Co(NH_3)_6I_3(s)$ is present all of the time.

Since we measured the solubility spectrophotometrically, we found it worthwhile to make a brief check of the spectra reported by Eve and Hume[2] and also extend these measurements to higher $[I^-]$. Instead of adding a reducing agent, we used oxygen-free solutions.

Data Analyses

Consider a solution saturated with $Co(NH_3)_6BiI_6(s)$ and $Co(NH_3)_6I_3(s)$. The two solubility products

$$K_s = [Co(NH_3)_6{}^{3+}][Bi^{3+}][I^-]^6$$

and

$$K_s' = [Co(NH_3)_6{}^{3+}][I^-]^3$$

give

$$K = K_s/K_s' = [Bi^{3+}][I^-]^3 \tag{1}$$

The solubility, S, is the total bismuth concentration

$$S = [Bi^{3+}] + \sum_{n=1}^{N} [BiI_n{}^{(3-n)+}]$$

Thus

$$S = K[I^-]^{-3}(1 + \sum_{n=1}^{N} \beta_n[I^-]^n)$$

where β_n is the stability constant for the nth complex. Introducing $\bar{n}$, the average ligand number, it may be shown that (*cf.*, *e.g.*, ref 5)

$$(d \log S)/(d \log [I^-]) = \bar{n} - 3 \tag{2}$$

From the slope of a curve $\log S$ *vs.* $\log [I^-]$, $\bar{n}$ is thus easily found. In the case when only $BiI_6{}^{3-}$ and one higher complex $(6 + m)$ are present, $\bar{n} = (6 + (6 + m)K_{6+m}[I^-]^m)/(1 + K_{6+m}[I^-])$ or

$$f_m = (\bar{n} - 6)/(6 + m - \bar{n}) = K_{6+m}[I^-]^m$$

where $K_{6+m} = \beta_{6+m}/\beta_6$. A plot of f_m *vs.* $[I^-]^m$ will yield a straight line with the slope K_{6+m}, if the correct value of m is chosen.

Experimental Section

Materials.—Only analytical grade chemicals were used. Hexaamminecobalt nitrate was dissolved in water and the yellow iodide was precipitated and washed with $4\ M$ sodium iodide. The precipitate was dissolved in hot water again and the whole procedure then repeated twice. Bismuth iodide was prepared from the chloride by slow addition of $4\ M$ NaI solution to $0.1\ M$ $BiCl_3$ in dilute HCl. BiI_3 was filtered, then repeatedly dissolved in $4\ M$ sodium iodide, and precipitated upon dilution. Finally, the bismuth iodide ($\sim 0.1\ M$), dissolved in $4\ M$ NaI, was added to a slight excess of the hexaamminecobalt(III) iodide, dissolved in water, whereupon the orange $Co(NH_3)_6BiI_6(s)$ formed. The solid was transferred to the Brønsted saturator. For details

about the operation of the saturator and the preparation of oxygen-free solutions, see ref 5g. The saturator was masked with tape to protect the cobalt salt from light. No indication of any serious light sensitivity was observed, however.

For spectrophotometric studies, oxygen-free solutions of known bismuth concentrations and varying $[I^-]$ were prepared from weighed amounts of $BiI_3(s)$.

Analyses.—Measurements were performed with a Beckman DU-2 spectrophotometer. With known bismuth concentrations, spectra were recorded between 400 and 500 mμ. Solubilities were measured as $[Bi(III)]$ at the isosbestic point at 455 mμ. Solvent was recycled through the salt bed until successive analyses showed no change in $[Bi(III)]$ as a test for achieving equilibrium. All solutions were measured without dilution in 1.0-mm cells open to the air. As a reference, solutions of the same composition, but without bismuth, were used. No change in the absorbance was found within 2 hr or more. All measurements were repeated at least twice. The solubilities could be reproduced to within 0.3%.

Choice of Concentrations.—In order to reach high ligand concentrations a $4\ M$ medium was chosen. $[I^-]$ ranged from 1 to 3.8 M for the spectral study and from 1.6 to 3.5 M for the solubility study. At these high concentrations, the risk of bismuth hydrolysis is small, and a low acidity, $0.01\ M$, was chosen. The supporting electrolyte was made up of Na^+ and $ClO_4{}^-$ ions.

The solubility of $Co(NH_3)_6I_3(s)$ was checked in 2 M iodide. At 455 mμ, no absorbancy due to cobalt was found ($A \leq 0.003$ in 10-mm cells). Thus, no correction of the bismuth absorbancies needed to be made in the range studied.

Solubility equilibria were attained at $25 \pm 0.1°$, and spectra were measured at $25 \pm 0.3°$.

Results and Discussion

We found, as expected, spectra with very much the same features as those of Eve and Hume.[2] Thus, at most wavelengths there is a slight, continuous change over the whole range of $[I^-]$, from 1 to 3.8 M. At 455 mμ, the isosbestic point, we obtained the absorbancy 0.648 ± 0.002 for $6.05 \times 10^{-5}\ M$ bismuth concentration, corresponding to a molar absorbancy of 10,700 M^{-1} cm^{-1}.

The results of the solubility study are shown in Table I. As $\bar{n}$ varies only slightly, it was considered sufficient to set $\Delta \log S/\Delta \log [I^-] = \bar{n} - 3$ for each interval (*cf.* eq 2) and consider as the corresponding value of $[I^-]$ the arithmetic mean of the two $[I^-]$ values. For the same reason, no correction of $[I^-]$ due to the solubility was considered necessary.

As is seen, $\bar{n}$ is very slightly but nevertheless significantly higher than 6. Moreover, there is, as expected, a tendency for $\bar{n}$ to rise. Despite the accuracy of the solubilities, the $\bar{n}$ values are not well suited for the accurate calculation of a constant. It is not even possible to conclude whether $BiI_7{}^{4-}$ or $BiI_8{}^{5-}$ is formed.

The spectral changes,[2] as well as the deviation of $\bar{n}$ from 6 in the solubility study, are both very small and could possibly be explained as medium effects. For instance, a lack of constancy in a solubility product could naturally invalidate our interpretation of the solubility data. However, iodides in perchlorate media are usually found to have constant solubility products at constant ionic strength.[5g,7,8] Moreover the fact that the two completely independent methods, spectrophotometric[2] and solubility, both clearly indicate

(7) R. O. Nilsson, *Arkiv Kemi*, **10**, 363 (1957).
(8) I. Leden, *Acta Chem. Scand.*, **10**, 540 (1956).

TABLE I
SOLUBILITIES OVER $Co(NH_3)_6BiI_6(s)$ AND $Co(NH_3)_6I_3(s)$

$[I^-]$, M^{-1}	Obsd	$10^2 S$, M^{-1} Calcd[a]	Calcd[b]	$\bar{n}$
1.6	0.1565	0.1555	0.1565	
				6.03
1.8	0.223	0.225	0.226	
				6.10
2.0	0.309	0.309	0.309	
				6.09
2.3	0.477	0.478	0.477	
				6.08
2.6	0.697	0.694	0.694	
				6.11
3.0	1.088	1.088	1.090	
				6.12
3.5	1.762	1.768	1.780	

[a] $K_7 = \beta_7/\beta_6 = 0.05$; $S = 3.51 \times 10^{-5}[I^-]^3(1 + K_7[I^-])$.
[b] $K_8 = \beta_8/\beta_6 = 0.009$; $S = 3.73 \times 10^{-5}[I^-]^3(1 + K_8[I^-]^2)$.

a complex with $\bar{n} > 6$ strongly supports the view that such a complex really exists.

However, since the effects due to the highest complex are so small, it seems unlikely that it will be possible to determine conclusively the number of iodides in the complex, or its formation constant. Eve and Hume[2] chose BiI_7^{4-}, stating that they got consistent constant values at different wavelengths only with this complex. We cannot agree with this conclusion, however, for the following reason. Although no primary data are given in the paper of Eve and Hume, it is possible to calculate, for different wavelengths, absorbancy values for their five upper ligand concentrations, from the values of K_7, A', and A'' in Table II and from Figure 6 of their paper. These should be close to their measured values. Now, using *one* value of K_8, we can find values of A' and A'' at all wavelengths, so that a set of absorbancies is obtained that never differs from the previous set by more than 0.3%. This shows clearly that it is not possible to conclude from their data whether BiI_7^{4-} or BiI_8^{5-} is formed.

TABLE II
VARIOUS INTERPRETATIONS OF THE DATA OF EVE AND HUME,[2] AT 402.5 mμ[a]

$[I^-]$, M	Obsd Ref 2, Figure 3	Calcd $K_7 = 0.13$	Calcd $K_7 = 0.01$	Calcd $K_8 = 0.024$
0.4	0.657	0.656	0.658	0.658
0.8	0.673	0.673	0.673	0.672
1.0	0.681	0.681	0.680	0.680
1.2	0.688	0.688	0.688	0.689
1.4	0.696	0.694	0.695	0.695

[a] Similar agreement is obtained at wavelengths 337 and 465 mμ.

We also feel the choice of value for K_7, based on Figure 4 in the paper of Eve and Hume, is tenuous. The value $K_7 = 0.077$ is rejected because the point of highest A deviates from the straight line for this value. A closer inspection of this point reveals, however, that a change of A (or A'') as small as 0.001 is sufficient to move the point to the line. Certainly, the absorbancy is not determined to better than 0.001. Thus, the only fact shown is that this point is not relevant, for

the purpose of Figure 4, for the determination of K_6. Points of higher $[I^-]$ are even less relevant, naturally.

As to K_7, the fact is that sets of absorbancies can be calculated at any wavelength with K_7 as different as 0.13 and 0.01 with a consistency within 0.3%, for the five relevant (highest) $[I^-]$ (Table II). Admittedly, though, the differences in spectra for BiI_6^{3-} and BiI_7^{4-} come out rather high for $K_7 = 0.01$, and for this reason a value $K_7 \approx 0.1$ seems more likely. It should also be noted that for the two ionic strengths, 2 and 4 M, a difference in the constant is to be expected.

To sum up, both investigations show that a complex BiI_n^{3-n} with $n > 6$ is formed. It is not possible, however, to conclude whether this complex is BiI_7^{4-} or BiI_8^{5-} nor to assign any very accurate value to the formation constant of the complex.

It is puzzling that data of this kind are indecisive concerning BiI_n^{3-n} complexes with $n > 6$, whereas similar data involving solubility equilibria lead clearly to postulation of $BiBr_8^{5-}$ [5e] and SnI_8^{6-}.[5g]

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Abnormal Mass Spectra of Nickel Schiff Base Chelates

BY EMILY P. DUDEK, ELEANOR CHAFFEE, AND GERALD DUDEK

Mass spectrometry has become an important analytical method in the investigation of inorganic compounds,[1,2] particularly in the determination of molecular weight. A knowledge of its limitations is essential for an intelligent application of the method. We, therefore, wish to report systems where the analysis of mass spectral data could easily lead to an erroneous identification of the molecular species originally present.

Complexes of nickel(II) with Schiff bases formed from salicylaldehyde and N-substituted ethylenediamines, $[Salen-N(R)R']_2Ni^{II}$, have been studied by Sacconi, Holm, and their coworkers.[3,4] Chemical, spectral, and magnetic measurements indicate that $[Salen-N(H)C_6H_5]_2Ni^{II}$ is a square-planar, four-coordi-
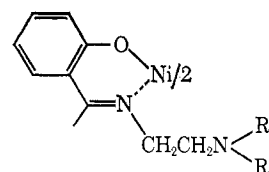
(1) C. Reichert, J. B. Westmore, and H. D. Gesser, *Chem. Commun.*, 782 (1967), and references contained therein.
(2) J. M. Smith, K. Mehner, and H. D. Kaesz, *J. Am. Chem. Soc.*, **89**, 1759 (1967).
(3) L. Sacconi, P. Nannelli, and U. Campigli, *Inorg. Chem.*, **4**, 818 (1965); L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *ibid.*, **4**, 943 (1965).
(4) A. Chakravorty, J. P. Fennessey, and R. H. Holm, *ibid.*, **4**, 26 (1965).