that the rate of decomposition was more rapid than the rate of exchange, then only the metal tetrachloride and the phosphoryl halide were obtained as decomposition products.

At the melting points of the $POF_2Cl \cdot MCl_4$ and $POF_3 \cdot MCl_4$ compounds, however, the metal tetrahalide was fluorinated as evidenced by the fact that the non-volatile residues resulting from the thermal decomposition were always high in fluorine and low in chlorine. Fluorination with phosphoryl fluoride was also observed when the initial reaction mixture was warmed up to −15° under pressure. For this reason the reactions with phosphoryl fluoride were carried out at −40°.

No significant difference in the behavior of zirconium and hafnium compounds was noted except that the hafnium compounds usually melted at slightly higher temperatures than the corresponding zirconium compounds.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Studies Pertaining to Soluble Silver Iodide Species

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The increase of the solubility of silver(I) iodide with an increasing concentration of silver(I) ion or iodide ion indicates the existence in solution of cationic and anionic complex ions. Solubility measurements, ion mobility determinations, and spectral studies have been employed to elucidate the nature of these complex ions. These studies indicate the existence of anionic complex ions which contain varying numbers of silver(I) ions and the existence of cationic complex ions which contain varying numbers of iodide ions. It appears that the solutions contain not merely monomeric and dimeric species but a large variety of these polymeric species.

In this work solubility measurements, ion mobility determinations and spectra studies have been utilized for the purpose of elucidating the equilibria which exist in solutions containing silver (I) and iodide. It will be seen that a wide variety of soluble species containing silver(I) and iodide must exist. While the methods utilized here are inadequate in completely describing the system, several important conclusions can be drawn from the observations.

Solubility Studies

The manner in which the solubility of a slightly soluble compound is affected by the concentration of a complexing agent provides valuable information regarding the species existing in the solutions. The interpretation is particularly straightforward if each of the soluble species contains only one ion or atom of the one kind. In the case of the solubility of silver(I) iodide in solutions of sodium iodide, the various possible equilibria would be

$$AgI(s) + nI^- \rightleftarrows AgI_{1+n}^{-n}$$

and the dependence of the solubility on the iodide ion concentration in media in which the activity coefficients could be assumed to be constant would allow a calculation of the average value of n, the charge on the complex. If the value of n is known as a function of the iodide concentration, the formulas of the species existing in solution over that concentration range can be established. If several complex species containing different numbers of silver(I) ions[1] exist, the situation is more complicated. The dependence of the solubility on the iodide ion concentration still gives the average value of the charge on the complex but no information regarding the number of silver(I) ions per unit is provided. If complexes containing varying numbers of silver(I) ions do exist, the solutions saturated with silver(I) iodide will have as important a contribution from the species containing the largest numbers of silver(I) ions as is possible for any solution of that particular iodide ion concentration.

W. Erber[2] has studied the solubility of silver(I) iodide in aqueous solutions of hydrogen iodide and found the solubility to be proportional to the fourth power of the iodide concentration over a wide concentration range. The interpretation that the species $Ag_2I_6^{-4}$ was present in the saturated solutions is of rather dubious validity. The ionic strength was not held constant and therefore the activity coefficients of the various species were not constant. No evidence was presented to prove the existence of a species containing a single number of silver(I) ions.

In an attempt to remove one of the factors contributing to the uncertainty in interpretation, the solubility of silver(I) iodide has been measured in media of varying sodium iodide concentration and approximately constant ionic strength (2 molar) at approximately 25°. This device of maintaining the ionic strength constant is not, of course, assurance that the activity coefficients of all of the species will remain constant.[3] In these studies the ionic strength was maintained constant with sodium perchlorate; calculations using the equation developed by Glueckauf[4] indicate that the mean activity coefficient of sodium iodide varies

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(1) The bonding in the silver(I) iodide complex ions undoubtedly has a great deal of covalent character. In this paper, the constituents of the complex ions will be referred to as silver(I) ions and iodide ions, nevertheless.

(2) W. Erber, *Z. anorg. allgem. Chem.*, **248**, 36 (1941).

(3) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," second ed., Reinhold Publishing Company, New York, N. Y., 1950, pp. 454-461.

(4) E. Glueckauf, *Nature*, **163**, 414 (1949).

about 15% over the concentration range employed in these solubility determinations. The results of these experiments are presented in Table I and Fig. 1. The interpretation of these data to yield the charge on the soluble species is possible only at lower concentrations of iodide for it is only under these concentration conditions that the actual concentration of iodide is approximately the same as the total concentration of iodide. At high concentrations of iodide, the amount of iodide tied up in the complex ions becomes appreciable compared to the total amount. The actual concentration of iodide in the saturated solutions can be calculated from knowledge of the average charge on the complex ions in a given solution and the solubility only if the number of silver(I) ions associated in the complex ions is known. The average charge on the soluble species is approximately -2 at the low iodide concentration limit regardless of the number of silver(I) ions assumed per ion-molecule. At the high iodide concentration limit, a charge of -3 to -4 is calculated if one assumes a very large number of silver(I) ions per ion-molecule and a value more negative than -7 if one assumes that the soluble species contain only one silver(I) ion per ion molecule. This, in itself, can be viewed as evidence that complex ions which contain more than one silver ion are the predominant species which exist in the saturated solutions of iodide concentration greater than approximately one molar. Polymeric species may also exist in the saturated solutions of lower iodide concentration but the average charge on the species in such solutions is not unreasonable and thus it cannot be stated that the solubility data lead to this conclusion.

TABLE I

SOLUBILITY OF SILVER IODIDE IN SOLUTIONS OF SODIUM IODIDE AND SODIUM PERCHLORATE

Temperature 24–26°; ($NaClO_4$) = 2.0 − (NaI) in moles/liter

Total iodide in moles/liter	Solubility, g. atom Ag/liter	Total iodide in moles/liter	Solubility, g. atom Ag/liter
0.118	7.6×10^{-5}	0.641	3.59×10^{-3}
.122	6.4	.766	6.14
.134	8.5	.942	1.05×10^{-2}
.172	1.39×10^{-4}	1.06	1.42
.184	1.59	1.17	2.05
.194	1.60	1.33[a]	2.94
.234	2.51	1.34	3.24
.277	3.84	1.42	3.69
.284	4.17	1.52	4.68
.362	7.63	1.72	6.73
.367	8.32	1.75	6.40
.437	1.26×10^{-3}	1.80	7.61
.461	1.46	1.86	8.39
.494	1.76	1.91	8.64
.584	2.70	2.11[a]	12.1

[a] In these experiments silver iodide was dissolved in sodium iodide solution; the concentration of sodium iodide given in the table is actually the sum of the concentrations of sodium iodide and silver iodide.

The measurements by Hellwig[5] of the solubility of silver(I) iodide in solutions of silver(I) nitrate demonstrate the existence of cationic complex ions. The linkage in these species is presumably the same as in the anionic species.

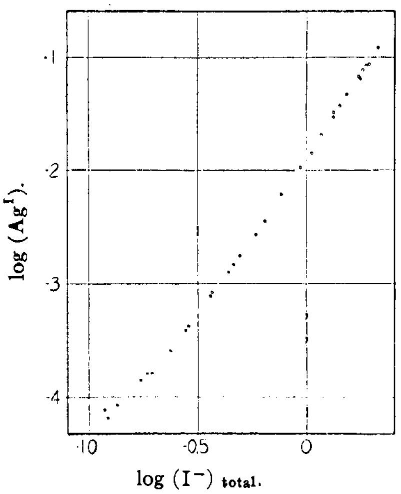

Fig. 1.—Logarithm of the solubility of silver(I) iodide *versus* logarithm of the total concentration of iodide ion: ionic strength: approximately 2; temp. approximately 25°.

Ion Mobility Determinations

The complex ions which exist in the presence of excess iodide ion have been referred to as anionic while those which exist in the presence of excess silver(I) ion as cationic. The sign of the charge on the complex ion is not open to question if they contain only silver(I) ions and iodide ions. A comparison of our solubility data (measured in the presence of sodium ion and no hydrogen ion) with those of Erber[2] (measured in the presence of hydrogen ion and no sodium ion) strongly suggests that neither sodium ion nor hydrogen ion are present in the anionic species. It is reasonable to assume that neither nitrate ion nor perchlorate ion are present in the complex ions.

To this knowledge of the sign of the charge on the predominant species has been added the values of the constituent mobility of silver(I) and iodide in media containing excess iodide ion and silver(I) ion, respectively. The constituent mobilities of silver(I) and iodide have been determined at 0° in a manner analogous to that used in the study of the constituent mobilities of cadmium(II) and iodide.[6] Solubility limitations prevent any such complete investigation as was carried out in the case of cadmium iodide. The anionic constituent mobility of silver(I) was determined in measurements on the boundary system: ~ 0.0025 M AgI, 0.61 M NaI(α) $\leftarrow$ NaI(β)::0.55 M NaI(γ).[7] It was observed that in this medium at 0°, the constituent mobility of silver(I) is -30×10^{-5} cm.^{2} volt^{-1} sec.$^{-1}$. This is to be compared with the values[6]: -25.0×10^{-5} for $HgI_4^{=}$ in 0.4 NaI and -28.2×10^{-5} for $CdI_4^{=}$ in 0.1 M NaI. The value of the constituent mobility of silver(I) suggests that the average charge of the silver(I) containing species is more negative than -2. The exact interpretation of the mobility data to yield the average value of the charge on the complex

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(5) K. Hellwig, *Z. anorg. Chem.*, **25**, 157 (1900).

(6) R. A. Alberty and E. L. King, THIS JOURNAL, **73**, 517 (1951).

(7) The moving boundary systems are represented by the notation of Longsworth, *ibid.*, **67**, 1109 (1945).

ions is not possible; no adequate theory exists which relates the mobility of an ion of uncertain shape, mass, and hydration with the ionic charge. The constituent mobility of iodide in the presence of excess silver(I) ion has been determined in measurements on the boundary system: 0.60 *M* $AgNO_3(\gamma)::AgNO_3(\beta) \rightarrow \sim$ 0.0021 *M* AgI, 0.65 *M* $AgNO_3(\alpha)$. The constituent mobility of iodide was found to be $+12.4 \times 10^{-5}$ cm.^{2} volt^{-1} sec.$^{-1}$. At first sight this value seems surprisingly low[8]; the value for hydrated cadmium ion is 19.3×10^{-5}.[6] The work on cadmium iodide indicated, however, that the magnitude of the mobility of a cation of charge +2 in which the first coördination sphere is occupied by water molecules is considerably lower than that of the anion of charge −2 in which the first coördination sphere around the central metal ion is occupied by four iodide ions. This suggests a reason for the low value of the mobility of the cationic silver(I) iodide species. The periphery of these complex ions is made up of silver(I) ions to which are associated water molecules. An ion with such an exterior might be expected to have a mobility which is low for its charge.

Spectra Studies

If the absorption of light by a particular constituent in a series of solutions does not obey Beer's law, one may conclude that there exist in the solutions one or more equilibria which are shifted with dilution. Although an equilibrium such as

$$AgI_4^{=} \rightleftarrows AgI_3^{=} + I^-$$

would shift upon dilution with water, no shift would occur upon dilution with a solution having the same concentration of iodide ion that existed in the original solution. In general, the ratio of the concentrations of any two silver(I) iodide complex ions which contain the same number of silver(I) ions will be a function of the iodide ion concentration but not of the silver(I) ion concentration. On the other hand, an equilibrium such as

$$2Ag_3I_n^{+3-n} + aI^- \rightleftarrows 3Ag_2I_{(2n+a)/3}^{+2-(2n+a)/3}$$

will shift upon dilution with a solution of iodide ion of the same concentration regardless of the value of *n* and *a*. It is clear that deviations from Beer's law by solutions of constant iodide concentration but varying silver(I) concentration indicate the existence at appreciable concentrations in the solutions of species containing varying numbers of silver(I) ions. Since the solubility data already discussed provided no information relevant to the question of whether all of the complex ions contain the same number of silver(I) ions, spectra studies have been made. The results of these experiments are summarized in Fig. 2. It is seen that Beer's law is not obeyed; the values of $\bar{\epsilon}_{Ag}$, the apparent extinction coefficient, ($\bar{\epsilon}_{Ag} = (\log I_0/I)/(Ag^I)l$ where l is the cell path length and (Ag^I) is the total concentration of silver in gram atoms per liter) are not constant. The values of $\bar{\epsilon}_{Ag}$ at 295 mμ at the lowest concentrations studied (3 to 6×10^{-4} molar) are very close to being constant. This suggests that the predominant species at such a concentration of silver(I) ion in the presence of 2.00 molar iodide ion involves only one silver(I) atom. Studies at lower concentrations of silver(I) would be desirable but a practical limit is placed on how low a concentration of silver(I) can be studied at a given wave length by the length of the cells which are used and by the absorption due to the iodide which is present at such a relatively high concentration.

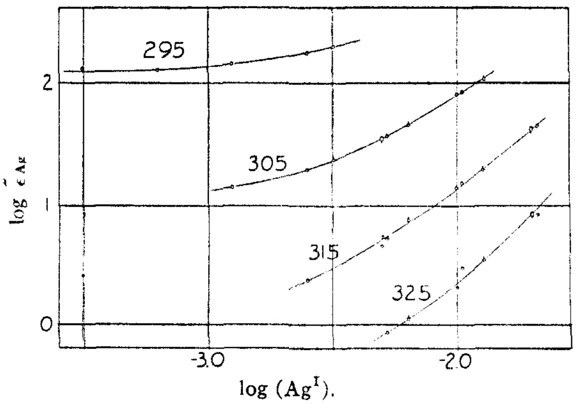

Fig. 2.—Logarithm of $\bar{\epsilon}_{Ag}$ *versus* logarithm of the concentration of silver(I). All solutions were 2.00 molar potassium iodide. The source of silver(I) is: O, silver nitrate solution; ⚲, silver perchlorate solution; ♀, solid silver iodide. The number adjacent to each curve is the wave length in mμ.

Since it has been shown[9] that the cadmium(II) iodide complex ions which are present in solutions of excess iodide ion contain only one cadmium(II) ion at cadmium(II) ion concentrations as high as 0.2 molar, it seemed desirable to determine the optical densities of solutions of cadmium(II) ion and iodide ion. In 2.0 molar potassium iodide, the molar extinction coefficient of cadmium(II) over the concentration range 4×10^{-2} to 5×10^{-3} molar is 7.7 ± 0.1 at 315 mμ. At this wave length and over a similar concentration range, the molar extinction coefficient of silver(I) varies twenty-fold. These data tend to confirm the monomeric nature of the cadmium(II) iodide complexes as well as rule out the possibility that an instrumental error is contributing significantly to the observed trends of $\bar{\epsilon}_{Ag}$ in the silver(I) iodide system.

It is seen that the value of $\bar{\epsilon}_{Ag}$ increases with increasing concentration of silver(I). This indicates that the absorption per silver(I) atom is greater the larger the size of the polymeric unit in which it exists. This is consistent with the qualitative discussion of light absorption by Pitzer and Hildebrand,[10] from which it would be expected that the wave length at which absorption occurs would become greater, the larger the absorbing electronic system becomes.

Measurements on solutions which were less concentrated in potassium iodide than 2.0 molar were also carried out. It was found that Beer's law was not obeyed under these conditions either. The relative values of $\bar{\epsilon}_{Ag}$ at constant silver(I) concentration are of interest. For example, at 315 mμ

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[8] The solubility data of Hellwig[5] suggest that the average charge on the cationic species is approximately +3 at 0.5 molar silver nitrate.

[9] I. Leden, *Z. physik. Chem.*, **188A**, 160 (1941).

[10] K. S. Pitzer and J. H. Hildebrand, THIS JOURNAL, **63**, 2472 (1941).

and a silver(I) concentration of 5.0×10^{-3} molar, the values of $\bar{\epsilon}_{\text{Ag}}$ are 125, 34 and 4.4 in solutions with a potassium iodide concentration of 0.9, 1.3 and 2.0 molar. Although the ionic strength varies in these three solutions, it seems unreasonable to ascribe the very large change in $\bar{\epsilon}_{\text{Ag}}$ to the salt effect on the spectrum of single species. The trend indicates that the equilibria between the several polymeric species shift with decreasing concentration of iodide to favor those species with a greater extinction coefficient, that is, those species with a greater number of silver atoms. This is consistent with the postulate that at a given iodide ion concentration, the fraction of the nearest neighbors of a silver(I) ion which is iodide ions is approximately the same regardless of the number of silver(I) ions which the unit contains. For if this is true and if the silver–silver bonding is by iodide bridges, iodide ion will necessarily appear on the product side of an equation for an equilibrium in which simpler units condense to give more complex units (*i.e.*, those with a larger extent of polymerization). Thus "dilution" at constant silver(I) concentration will shift the equilibria to form larger units which have been shown to have greater extinction coefficient values.

The question of whether the spectral data are consistent with the existence of only monomeric and dimeric species (*i.e.*, those containing only one and two silver(I) ions) has been investigated in the same manner as was used in the study of the spectra of cerium(IV) perchlorate solutions.[11] The data at wave lengths 305 and 325 mμ are not consistent with the existence of only monomeric and dimeric species. It seems reasonable to picture a great number of polymeric species existing in these solutions. Any one particular set of equilibrium constants and extinction coefficients which could be found to yield values of the optical density in agreement with experiment would not be a unique set of such parameters. It does not appear to be worthwhile, therefore, to attempt any numerical treatment of these spectral data. It can be said that the data prove that the anionic species which exist in the presence of excess iodide ion contain varying numbers of silver ions.

On the basis of the conclusions already reached regarding the anionic species which exist in the presence of excess iodide ion, it is reasonable to expect that the cationic species contain different numbers of iodide ions. This expectation is confirmed by data on the light absorption of undersaturated solutions of potassium iodide in 1.20 molar silver(I) perchlorate. The values of $\bar{\epsilon}_{\text{I}}$ ($\bar{\epsilon}_{\text{I}} = (\log I_0/I)/(\text{I}^-)l$) as a function of the concentration of iodide ion are presented in Fig. 3. It is seen that Beer's law is definitely not obeyed although the variations of the values of $\bar{\epsilon}_{\text{I}}$ are much smaller than those observed for $\bar{\epsilon}_{\text{Ag}}$. This may indicate that the difference between the values of the extinction coefficients of the anionic species containing successive numbers of silver(I) ions is much greater than between the extinction coefficients of the cationic species containing successive numbers of iodide ions.

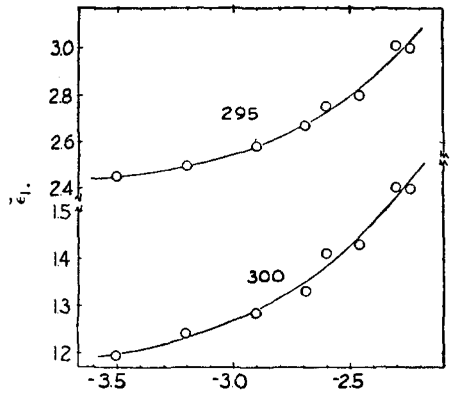

Fig. 3.—The value of $\bar{\epsilon}_{\text{I}}$ *versus* logarithm of iodide concentration. All solutions were 1.20 molar silver perchlorate. The number adjacent to each curve is the wave length in mμ.

Two facts confirm that the observed decrease in light transmission is due to true absorption and not the type of light scattering which is exhibited by solutions of high polymers. The extinction coefficients are enormously greater than could be possible if this were merely light scattering and the power dependence of $\bar{\epsilon}$ on $(1/\lambda)$ is about tenfold higher than the maximum value possible for the case of true turbidity.[12]

Experimental

Materials.—All solutions were prepared using doubly distilled water. The silver nitrate, sodium iodide and potassium iodide were reagent grade quality and were used without further purification. The sodium perchlorate was purified by recrystallization from water. The silver perchlorate solution was prepared by treating freshly precipitated and washed silver oxide with a measured, insufficient quantity of reagent grade perchloric acid solution. The excess silver oxide was removed by centrifugation.

The concentrations of the solutions were determined by standard analytical methods or in cases where compounds of known composition were used by the weight of the material used.

Solubility Studies.—Most of the solubility data were obtained in titration experiments at 25 ± 1°. Solutions containing silver(I) nitrate and sodium perchlorate of ionic strength equal to 2.0 were titrated into solutions of sodium iodide and sodium perchlorate of ionic strength equal to 2.0. In such a titration, solid forms when a drop of silver(I) solution enters the iodide solution; if the solution is undersaturated, the solid rapidly dissolves. If the solution is saturated, however, the solid persists. Under most of the concentration conditions studied, the point at which the solution became saturated was quite definite. Most experiments were done in triplicate and the three samples agreed within 0.5%. Solubility determinations were also made at 25° in quadruplicate at two concentrations of iodide ion by equilibrating solid silver(I) iodide prepared by the method of Baxter and Lundstedt[13] with a solution of sodium iodide in one case and a solution of sodium iodide and sodium perchlorate in another case. The silver iodide which had dissolved was reprecipitated by a ten-fold dilution of an aliquot of saturated solution. This solid was filtered in a sintered crucible, dried, and weighed. The duplicate determinations agreed to 1% at the higher iodide concentration and 4% at the lower concentration. These solubility data agree well with those determined in the titrations. The solubility of silver(I) iodide determined at an ionic strength close to 2.0 by Erber[2] agrees well with the solubilities measured in this work. Since Erber measured the solubility in solutions of hydrogen iodide, the agreement indicates that the solid in equilibrium with the solution containing

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[11] E. L. King and M. L. Pandow, THIS JOURNAL, **74**, 1966 (1952).

[12] W. Heller and E. Vassy, *J. Chem. Phys.*, **14**, 565 (1946).

[13] G. P. Baxter and O. W. Lundstedt, THIS JOURNAL, **62**, 1829 (1940).

both sodium iodide and sodium perchlorate contains no sodium ion.

Ion Mobility Determinations.[14]—The ion mobility determinations were carried out in the same manner as has been described elsewhere.[6] In the experiment in which the constituent mobility of iodide was determined, silver nitrate solution rather than sodium chloride solution was in contact with the silver–silver(I) chloride electrodes. The results presented were obtained in single runs at each set of concentration conditions. Pictures of the schlieren pattern were taken at several times during each run and the boundary velocities were found to be constant.

Spectra Studies.—Spectrophotometric measurements were made using a Beckman DU spectrophotometer equipped for maintaining the temperature of the solutions at approximately 25°. Cells of one cm. and ten cm. path lengths were used.

Most of the solutions studied were prepared using silver nitrate and potassium iodide. In some cases the solution in the blank cell contained potassium iodide but no nitrate ion. Since nitrate absorbs appreciably at some of the wave lengths studied, the observed absorption was corrected for this; the absorption by nitrate was determined in experiments in which potassium nitrate–potassium iodide solutions were measured against a potassium iodide solution as a blank. Some experiments were performed using silver perchlorate rather than silver nitrate. Since perchlorate ion absorbs much less than nitrate ion, no uncertainty exists regarding corrections for its absorption. In another series of experiments, silver(I) iodide which had been prepared for the direct solubility determinations and which had stood under water in a darkened cabinet for over a year was dissolved in potassium iodide solution. With certain exceptions to be discussed the values of $\bar{\epsilon}_{Ag}$ were the same within the experimental uncertainty regardless of which of these several methods of preparation of the solutions was used. This is indicated in Fig. 2 in which different symbols are used for the solutions prepared in the different ways.

Sodium thiosulfate was present in both sample and blank at approximately 5 to 10 × 10^{-4} molar. At this concentration it contributes negligibly to the absorption and does not compete effectively with iodide ion for complexing of silver(I); however, it does keep iodine in the reduced state. Because of its absorption, I_3^-, which would be formed by air oxidation, must be absent from the solutions.

In some experiments on solutions containing excess iodide in which silver nitrate or silver perchlorate was used, the absorption was determined at several different times (*e.g.*, at 1, 7 and 14 days after preparation). In general, the optical density readings were within a few per cent. of each other but in some cases, it was observed that the absorption at longer wave lengths (> 330 mμ) increased with increasing time by amounts greater than a few per cent. A reasonable explanation of this seems to be that reducing impurities, such as lint, were bringing about the slow formation of colloidal silver. The scattering of light by this material would be more important relative to the absorption by the complex ions at longer wave lengths.

In the case of the solutions prepared using the aged silver(I) iodide, it was observed that the absorption at wave lengths greater than 340 mμ was markedly greater at the time of preparation of the solution than was the absorption of a solution prepared using silver nitrate or silver perchlorate. The absorption at these wave lengths decreased with time. This behavior is consistent with the existence of a small but significant concentration of silver(I) iodide colloidal aggregates in solutions prepared in this way. These colloidal aggregates, which must be present in only small amounts since the absorption at shorter wave lengths is approximately the same as expected, slowly react with the medium to form the equilibrium polymeric species. It seems reasonable that this would occur in the solutions prepared using silver(I) which was initially present in the very large aggregate units existing in solid silver(I) iodide.

Discussion

The experimental data presented in this paper provide interesting information regarding the soluble species which exist in solutions containing silver(I) ion and iodide ion. It is not possible, however, to interpret any of these data to yield the exact composition of the several species and the several equilibrium quotients. An experimental technique which will yield such information is the measurement of electromotive force. While much work has been done on the silver–silver(I) iodide electrode potential, none appears to have been done on the silver–silver(I) potential in iodide solutions which are *not* saturated with silver(I) iodide. It is such measurements which will yield the average number of silver(I) ions per ion-molecule. At 25° in solutions of constant iodide concentration, a tenfold change in the silver(I) concentration will result in a change of the silver half-cell voltage of $0.059/n$ volts, where n is the average number of silver(I) ions per ion molecule.

This formation of soluble polymeric species has been observed in a number of metal ion–hydroxide ion (or oxide ion) systems but this type of behavior in the case of metal–halide complex ions does not seem to be as common. The large extent of covalent character in silver–iodide bonds[15] is undoubtedly one of the factors which stabilize these polymeric species in the case of silver iodide. These covalent forces, which contribute so markedly to the stability of solid silver iodide and lead to its very low solubility in pure water in which it dissolves to give the simple hydrated ions, are also present in these polymeric ion-molecules. The binding in these ion-molecules undoubtedly has a great deal in common with that in the solid.

It would not be surprising to find that species of this sort also exist in solutions of copper(I) iodide and gold(I) iodide in aqueous iodide solution. The extent to which such polymeric ion-molecules are present in solutions of the other silver(I) halides is not known. It would be expected to be less if the suggestion that the covalent nature of the binding in silver(I) iodide is an important factor in stabilizing such species is correct.

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(14) The authors wish to express their appreciation to Mr. E. B. Dismukes for assistance in performing these experiments and to Professors J. W. Williams and R. A. Alberty for the use of the equipment which was employed

(15) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1942, p. 73.