species. They are most likely solvated complexes of the type $Ni(solv)_6^{2+}$ and $Ni(solv)_5Br^+$, where "solv" represents a coordinated solvent molecule, in this case 2-methoxyethanol. The bands for the hexasolvated species occur at almost the same wave numbers as those of the hexaaquonickel(II) ion,[15] but have considerably higher intensity. This increase in intensity upon replacement of water molecules in the first coordination sphere of Ni^{2+} by other solvent molecules has been observed by several previous workers.[14,16-20]

The general spectral behavior reported here for 2-methoxyethanol, *i.e.*, shift of the absorption bands of Ni^{2+} to longer wave lengths upon addition of halide, accompanied by an increase in intensity, has been observed by other investigators in solvents such as alcohols,[2,21] dimethylformamide,[2,16,22] acetone,[5,9] and acetonitrile.[6,8,10] The spectral features were produced by adding small quantities of chloride or bromide to solutions of nickelous perchlorate,[5,6,8-10] by dissolving nickelous dihalides in the solvents,[21,22] and by increasing the temperature of nickel(II)–halide solutions.[2] Similar observations have been made for aqueous solutions highly concentrated in chloride or bromide.[23-26] Our results for 2-methoxyethanol indicate that this spectral behavior is probably ascribable to the formation of an octahedral monohalo complex.

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Solubility of Silver Halides and Stability of Silver Halide Complexes in Selected Nonaqueous Media

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The solubility product constants of AgCl, AgBr, and AgI and the over-all formation constants of AgX_2^- complexes have been investigated in acetonitrile, dimethyl sulfoxide, nitroethane, acetone, and methanol by potentiometric and voltammetric techniques. The solubility of each of the silver halides parallels the relative solvating ability of the solvents for silver ion as indicated by reduction potentials. In each solvent, the over-all formation constants of the AgX_2^- complexes increase from $AgCl_2^-$ to AgI_2^-. The tendency for the reaction $AgX(s) + X^- \rightleftharpoons AgX_2^-$ to occur is much less pronounced in methanol than in the other solvents. This is attributed to the ability of methanol to solvate halide ion through a hydrogen-bonding mechanism, thus making it less available for reaction with solid silver halide.

Introduction

Although extensive quantitative studies on the solubility of silver halides and the stability of silver halide complexes in water have been made, only a limited number of such investigations have been carried out in nonaqueous media. The data obtained from these latter studies have been summarized by Kratohvil and Težak[1] and Sillén and Martell.[2] Solubility product constants for the halides (except the fluoride) in methanol, ethanol, diethyl ether, and ethylenediamine have been reported. Data for the stability constants of AgX_2^- complexes are even more sparse, with only values for the $AgCl_2^-$ species in N-methylformamide and for the AgI_2^- complex in acetone, ether, and dimethylformamide being reported.

In this paper, we present the results of a systematic study of the solubility of silver chloride, bromide, and iodide and of the stability of the three AgX_2^- complexes in acetonitrile, dimethyl sulfoxide (DMSO), nitroethane, acetone, and methanol. These solvents were chosen to provide a wide spectrum of solvating ability toward both cation and anion.

Experimental Section

Materials.—Dimethyl sulfoxide, obtained from Crown Zellerbach, was purified by passage through a column of activated alumina, followed by fractional distillation under reduced pressure at a temperature below 70°, the first and last 10% of the distillate being discarded.[3] Karl Fischer titration showed the water content of the distillate to be about 0.02 *M*. Nitroethane (Aldrich Chemical Co.) was dried over Drierite for several weeks, passed through activated alumina, and distilled *in vacuo*. The fraction representing the middle 80% of the distillate was collected and found to be less than 0.002 *M* in water. Baker Analyzed reagent acetone, after being maintained over Drierite for several weeks, was fractionally distilled, the fraction boiling at 56° being collected. Infrared analysis showed the water concentration to be less than 0.05 *M*. Methanol was purified by

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treatment with calcium hydride and potassium borohydride, followed by fractional distillation through a 4-ft. column packed with glass helices. The fraction collected boiled within a 0.3° range and had a water content of less than 0.02 *M*. Matheson Coleman and Bell Chromatoquality acetonitrile was purified by distillation from phosphorus(V) oxide, followed by fractional distillation from calcium hydride, the fraction boiling at 82° being collected; the water content was less than 0.002 *M*. The usual precautions were taken to avoid exposure of solvents to the atmosphere.

Silver perchlorate (G. F. Smith Chemical Co.) was dried at 110° prior to use. Anhydrous lithium perchlorate (G. F. Smith Chemical Co.) was dissolved in water and, after passage through activated charcoal, was recrystallized and dried first at 80° and then at 180°. Reagent grade sodium iodide was dried at 110° *in vacuo*. Lithium chloride and lithium bromide, both reagent grade, were dried at 110° before use. Eastman White Label tetraethylammonium chloride was recrystallized from acetonitrile and washed with acetone. The product was then dried at 110°. Tetraethylammonium bromide (Eastman White Label) was recrystallized three times from acetonitrile, washed with ether, and dried under vacuum at room temperature. Eastman White Label tetrabutylammonium iodide, m.p. 144.5–145.5° (uncor.; lit.[4] 144°), was used without further purification. Solutions of the iodide in nitroethane were unstable and were used within 24 hr. of preparation. Tetrabutylammonium perchlorate was precipitated by addition of perchloric acid to the iodide in water. The crude salt was filtered, washed with water, and dissolved in acetone. The resulting solution was treated with silver perchlorate to remove iodide impurity. After filtration of silver iodide, a small amount of water was added to the acetone solution, and excess silver ion was removed by controlled potential electrolysis at −0.2 v. *vs*. s.c.e. The solution was then evaporated almost to dryness, and the tetrabutylammonium perchlorate was filtered off and washed with water until a suspension of the salt in water was neutral. The salt, dried *in vacuo*, melted sharply at 214° (uncor.); lit.[5] 210.5°. Methanol solutions (0.1 *M*) of tetrabutylammonium perchlorate gave satisfactory background scans with the rotating platinum and dropping mercury electrodes. Tetraethylammonium perchlorate was prepared by adding a slight excess of perchloric acid to a solution of tetraethylammonium bromide. The insoluble perchlorate was filtered off and recrystallized from water until a 0.1 *M* solution in acetonitrile showed no bromide oxidation wave.

All halide solutions were standardized by potentiometric titration with aqueous standard silver nitrate solution. Silver perchlorate solutions were standardized by addition of excess of standardized halide solution and back titration of unconsumed halide ion with standard silver nitrate solution.

Potentiometric Measurements.—The potentiometric measurements were carried out in a modified polarographic H cell. One of the side arms in the conventional cell was replaced by a 50-ml. erlenmeyer flask. A clean silver wire, which served as the indicator electrode, was placed in the flask. Potentials were read against the saturated aqueous calomel electrode with the use of a Leeds and Northrup Model 7664 pH indicator. A sintered-glass disk separated the erlenmeyer flask from the calomel electrode compartment and prevented gross mixing of the solutions. During the course of each experiment, anhydrous nitrogen presaturated with solvent was passed through the solution which was stirred magnetically. All measurements were carried out at room temperature, 23 ± 1°. The ionic strength was maintained at 1.00 *F* in methanol and 0.100 *F* in acetone with lithium perchlorate, and 0.100 *F* in acetonitrile, DMSO, and nitroethane with tetraethylammonium perchlorate. For the determination of the solubility product constant for each of the silver halides in each of the solvents, 25 ml. of silver perchlorate solution having a concentration in the range of about 10^{-4} to 10^{-3} *M* was titrated with halide solution approximately ten times as concentrated. For the evaluation of β_2 (the over-all formation constant for the complex AgX_2^-), the silver perchlorate solutions had concentrations ranging from about 2×10^{-5} to 10^{-3} *M*; in a titration of any one silver perchlorate solution, two or more halide solutions of greater concentration were used. Lithium chloride, lithium bromide, and sodium iodide were the sources of halide ion in methanol. In acetone, halide ion was supplied by lithium chloride, lithium bromide, and tetrabutylammonium iodide. Tetraethylammonium chloride, tetraethylammonium bromide, and tetrabutylammonium iodide were used in acetonitrile, DMSO, and nitroethane.

Voltammetric Measurements.—Values for β_2 were also determined by voltammetry. The current–voltage curves were obtained with a modified Kelley–Fisher–Jones controlled-potential polarograph.[6–8] A rotating platinum electrode was placed in one compartment of a conventional polarographic H cell, and a saturated aqueous calomel electrode and a platinum-foil electrode were placed in the other compartment. A platinum wire sealed in the end of a soft-glass tube served as the rotating electrode and during a measurement was rotated at about 600 r.p.m. with a Sargent synchronous rotor. The foil electrode was the auxiliary electrode in a three-electrode system. All current–voltage curves were obtained at a scan rate of 115 mv./min. or slower and at room temperature. Solutions were deaerated with nitrogen presaturated with solvent. The silver perchlorate solutions had concentrations ranging from about 4×10^{-5} to 10^{-4} *M*, and, depending on the particular solvent, the halide ion employed in an experiment varied in concentration by a factor between 10 and 100, with starting concentrations in the range of 10^{-3} to 10^{-1} *M*.

Calculations.[9]—The solubility product constants, $K_{sp} = [Ag^+][X^-]$, were calculated from the potentiometric titration curves by the use of the potentials at the equivalence points. The potential at the equivalence point, through the use of the Nernst equation, provides information on the silver ion concentration in a saturated solution of the silver halide. The formal potential for the Ag^+,Ag couple was evaluated from the initial potential reading before the addition of halide ion; in some cases, however, where the subsequent readings justified it, the potential reading after the addition of a small amount of halide was used. In methanol, in which the formation of dihalo complexes, AgX_2^-, is negligible, the solubility product is obtained by simply squaring the silver ion concentration at the equivalence point. In the other organic solvents used, the formation of dihalo complexes cannot be neglected, and correction for them must be made by the use of the relationship $[Ag^+] = [AgX_2^-] + [X^-]$. The concentration of the complex ion at the equivalence point can be obtained from β_2 values. (See below for evaluation of β_2). The precision of the calculated solubility product constants was $10^{\pm 0.2}$.

Calculations of solubility product values were also made from points beyond the equivalence point and before the complete conversion of silver halide to dihalo complex. No difference was observed between the results found in this manner and those obtained at the equivalence point. Thus, for example, in nitromethane the K_{sp} value for silver bromide calculated from the equivalence point potential was $10^{-21.8}$, whereas, from three points beyond the equivalence point, identical values of $10^{-21.7}$ were obtained.

Calculations of β_2 values were made both from potentiometric and voltammetric data. In each potentiometric analysis, constants were calculated at a number of points beyond that at which 2 equivalents of halide ion was added per equivalent of silver. The precision of the values obtained was $10^{\pm 0.2}$.

For the voltammetric determination of β_2 values, a modifica-

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tion of the equation derived by Cohen, Iwamoto, and Kleinberg[10] was utilized.

$$E_{1/2} = E^{\circ\prime} - (0.0591/n) \log \beta_p - (p0.0591/n) \times \log [\mathrm{X}^-] + (0.0591/n) \log ([\mathrm{AgX}_p{}^{-p+1}]/2)$$

In the above expression, $E_{1/2}$ is the potential at half the diffusion current, i_d, and $E^{\circ\prime}$ includes the standard potential of the silver couple and the activity coefficients of the silver ion and the complex at the electrode surface. The diffusion coefficients of the metal ion and the complex are assumed to be the same. The applicability of this expression was demonstrated by the fact that E (the potential at any point i on the current–voltage curve) *vs.* log ($i_d - i$) plots gave slopes which were close to the reversible value of 0.060—generally of the order of 0.07—with the shape of the wave becoming more nearly ideal as the concentration of halide ion decreased. The number of halide groups in the complex (p) was determined from plots of $E_{1/2}$ *vs.* 0.0591 log [X$^-$], and values between 1.8 and 2.2 were found. The precision of the β_2 values obtained was $10^{\pm 0.3}$.

The Nernst expression in the voltammetric work was checked usually over a tenfold concentration range of silver ion. The uncertainty in the $E^{\circ\prime}$ values ranged from 0.005 to 0.010 v.

Results and Discussion

The solubility product constants of the silver halides and the over-all formation constants (β_2) of the dihalo complexes in the various nonaqueous solvents investigated are summarized in Tables I and II, respectively.

TABLE I

SOLUBILITY PRODUCT CONSTANTS OF SILVER HALIDES IN NONAQUEOUS SOLVENTS[a] ($t = 23°$; $K_{sp} = [\mathrm{Ag}^+][\mathrm{X}^-]$)

Solvent	AgCl	AgBr	AgI
DMSO[b]	$10^{-10.4}$	$10^{-10.6}$	$10^{-12.0}$
Acetonitrile[b]	$10^{-12.4}$	$10^{-13.2}$	$10^{-14.2}$
Methanol[c]	$10^{-13.0}$	$10^{-15.2}$	$10^{-18.2}$
Acetone[d]	$10^{-16.4}$	$10^{-18.7}$	$10^{-20.9}$
Nitroethane[b]	$10^{-21.1}$	$10^{-21.8}$	$10^{-22.6}$

[a] In the calculation of the K_{sp} values, corrections for the formation of dihalo complexes were made with the use of β_2 values obtained by the voltammetric method. No corrections were necessary for the formation of dihalo complexes in methanol. [b] Ionic strength maintained at 0.100 F with $(\mathrm{C_2H_5})_4\mathrm{NClO_4}$. [c] Ionic strength maintained at 1.00 F with $\mathrm{LiClO_4}$. [d] Ionic strength maintained at 0.100 F with $\mathrm{LiClO_4}$.

Among the obvious factors of significance in determining the relative order of solubility of the silver halides and of the extent of their interaction with excess halide ion in a variety of solvents is the degree of solvation of the various ionic species present. The formal reduction potentials of silver ion in the various solvents (corrected for liquid junction potential differences) generally may be used to evaluate the relative order of solvation of that ion; a more negative potential indicates a greater degree of solvation. For the solvents used in our study, the formal reduction potentials indicate that the degree of solvation of silver ion increases in the order: nitroethane < acetone < methanol < acetonitrile < DMSO (0.61, 0.40, 0.34, 0.13, 0.03 v.).[11] It is evident from the data of Table I that the solubility of each of the silver halides parallels the relative solvating ability of the solvents for silver ion as indicated by reduction potentials. This fact strongly suggests that in these solvents cation–solvent interaction plays a greater role than anion–solvent interaction in determining the solubility of silver halides. In each solvent the order of decreasing solubility is, as expected, AgCl > AgBr > AgI.

TABLE II

THE OVER-ALL FORMATION CONSTANTS (β_2) OF DIHALO COMPLEXES OF SILVER IN NONAQUEOUS SOLVENTS ($t = 23°$· $\beta_2 = [\mathrm{AgX_2}^-]/[\mathrm{Ag}^+][\mathrm{X}^-]^2$)

Solvent	$\mathrm{AgCl_2}^-$ Potentiometric	$\mathrm{AgCl_2}^-$ Voltammetric	$\mathrm{AgBr_2}^-$ Potentiometric	$\mathrm{AgBr_2}^-$ Voltammetric	$\mathrm{AgI_2}^-$ Potentiometric	$\mathrm{AgI_2}^-$ Voltammetric
DMSO[a]	$10^{11.9}$	$10^{12.1}$	$10^{11.7}$	$10^{12.3}$	$10^{13.1}$	$10^{13.2}$
Acetonitrile[a]	$10^{12.6}$	$10^{13.6}$	$10^{13.4}$	$10^{14.1}$	$10^{14.6}$	$10^{15.7}$
Methanol[b]	$10^{8.0}$	$10^{7.7}$	$10^{10.9}$	$10^{10.2}$	$10^{14.8}$	$10^{14.8}$
Acetone[c]	$10^{16.7}$	$10^{16.7}$	$10^{19.7}$	$10^{20.2}$	$10^{22.2}$	$10^{22.3}$
Nitroethane[d]	$10^{22.2}$	$10^{22.5}$	$10^{22.5}$	$10^{22.4}$	$10^{23.5}$	$10^{23.6}$

[a] Ionic strength maintained at 0.100 F with $(\mathrm{C_2H_5})_4\mathrm{NClO_4}$. [b] Ionic strength maintained at 1.00 F with $\mathrm{LiClO_4}$. [c] Ionic strength maintained at 0.100 F with $\mathrm{LiClO_4}$

Because the solvents investigated cover a limited and intermediate range of dielectric constant (acetone, 21; nitroethane, 28; methanol, 33; acetonitrile, 38; and DMSO, 47; all at 25°), no obvious effect of this factor on solubility is evident.

In each solvent, the over-all formation constants of the dihalo complexes (β_2) increase from $\mathrm{AgCl_2}^-$ to $\mathrm{AgI_2}^-$. For the effect of solvent on the formation of these complexes, one must consider the reaction $\mathrm{AgX(s)} + \mathrm{X}^- \rightleftharpoons \mathrm{AgX_2}^-$. The equilibrium constants for this reaction are found from the ratio K_{sp}/β_2. The values for these equilibrium constants for chloride, bromide, and iodide are, respectively: acetonitrile, $10^{0.2}$, $10^{0.2}$, $10^{0.4}$; DMSO, $10^{1.5}$, $10^{1.1}$, $10^{1.1}$; nitroethane, $10^{1.1}$, $10^{0.7}$, $10^{0.9}$; acetone, $10^{0.3}$, $10^{1.0}$, $10^{1.3}$; and methanol, $10^{-5.0}$, $10^{-4.3}$, $10^{-3.4}$. (The β_2 values used were those found by the potentiometric technique.) It is evident that the tendency for the reaction noted above to take place is much less pronounced in methanol than in the other solvents. The great difference in behavior can undoubtedly be attributed to the ability of methanol to solvate the halide anion through a hydrogen-bonding mechanism and thus make it less available for interaction with solid silver halide. Clearly, the large $\mathrm{AgX_2}^-$ anion is relatively insensitive to the effect of hydrogen bonding.

It should be noted that the constants reported are formal ones in the sense that no correction for the presence of ion-pair species, *e.g.* (Li^+, $\mathrm{AgCl_2}^-$) and ($(\mathrm{C_2H_5})_4\mathrm{N}^+$, Cl^-), has been made because of the unavailability of the appropriate data for all of the solvents. In the case of β_2 values in acetonitrile where the ion-pair formation constants for $(\mathrm{C_2H_5})_4\mathrm{N}^+\mathrm{ClO_4}^-$, $(\mathrm{C_2H_5})_4\mathrm{N}^+\mathrm{Cl}^-$, and $(\mathrm{C_2H_5})_4\mathrm{N}^+\mathrm{Br}^-$ are available,[12] cor-

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rection for ion-pair formation between $(C_2H_5)_4N^+$ and anions by the use of $K_{(C_2H_5)_4N^+ClO_4^-} = 10^{1.05}$, $K_{(C_2H_5)_4N^+Cl^-} = 10^{1.54}$, and $K_{(C_2H_5)_4N^+Br^-} = 10^{1.35}$ changed the constant obtained by potentiometry for $AgCl_2^-$ from $10^{12.6}$ to $10^{13.6}$, and that for $AgBr_2^-$ changed from $10^{13.4}$ to $10^{14.1}$. The constants obtained by voltammetry were increased from $10^{13.6}$ to $10^{14.7}$ for $AgCl_2^-$ and from $10^{14.1}$ to $10^{14.8}$ for $AgBr_2^-$.

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Far-Infrared Spectra of Oxochloro and Oxobromo Complexes of Nb(V), Mo(V), and W(V)

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The infrared spectra of the compounds $A_2[MOX_5]$, where A = Rb or Cs, M = Nb, Mo, or W, and X = Cl or Br, have been determined in the range 1000–80 cm.$^{-1}$. An assignment of the observed bands is presented.

Introduction

Although the far-infrared spectra of a number of metal halo complexes have been reported,[1–7] the study of oxohalo complexes has been limited to the M–O stretching vibration,[8] which occurs in the sodium chloride region. No Raman spectra of these ions have been reported in the literature. The present study extends the measure of the infrared spectrum down to 80 cm.$^{-1}$ and was undertaken in order to obtain more complete information about the vibrational spectra of the complex ions $[MOX_5]^{2-}$ where M = Nb, Mo, or W and X = Cl or Br.

Experimental Section

The compounds were prepared by standard methods[9] and were analyzed for halogen content. The spectra were recorded on Perkin-Elmer Model 337, 421, and 301 spectrophotometers. Mulls of the solids in Nujol were used to obtain spectra above 400 cm.$^{-1}$, whereas pressed polythene disks were used below this frequency. Spectra in the far-infrared region were recorded both at room temperature and at low temperature. The temperature of the disks, measured by means of a thermocouple in contact with it, varied between −150 and −160°.

Results

Figures 1 and 2 report two typical spectra of oxochloro and oxobromo complexes in the far-infrared region. Since some of the bands are rather diffuse at room temperature (A spectra in Figures 1 and 2), the spectra were also run at *ca.* −155° in the hope that overlapping bands might be resolved, but though a sharpening was clearly evident at the lower temperature (B spectra in Figures 1 and 2), the broad bands were only rarely resolved into more than one component. The frequencies of the absorption bands observed in the low-temperature spectra are given in Table I.

Discussion

The complex ions $[MOX_5]^{2-}$ belong to the point group C_{4v} in which the fifteen normal modes of vibration span the representations $4A_1 + 2B_1 + B_2 + 4E$. Only the species of A_1 and E symmetry are infrared active. The four A_1 species can be described approximately as a M–O stretching, two M–X stretching, and one X–M–X, O–M–X deformational mode; the four E species as one M–X stretching and three X–M–X, O–M–X bending modes. Taking into consideration the relative masses and bond strengths one of the degenerate modes can be approximately described as a M–O rocking mode.

Reported M–X stretching and X–M–X bending frequencies can be used as a guide to the assignment of these frequencies in the oxohalo complexes. Thus, the bands observed at *ca.* 320 cm.$^{-1}$ in the oxochloro complexes are assigned to the M–Cl stretching mode by comparison with the frequencies of 330 cm.$^{-1}$ in $M_2[MoCl_6]$ and 310 cm.$^{-1}$ in $M_2[WCl_6]$[4]; the bands at *ca.* 170 cm.$^{-1}$ are attributed to the Cl–M–Cl deformational modes ($[MoCl_6]^{2-}$ 170 cm.$^{-1}$, $[WCl_3]^{2-}$ 160 cm.$^{-1}$).

Two further bands were found in the spectra of the oxochloro complexes at *ca.* 230 cm.$^{-1}$. These are designated as the M–O rocking frequencies, no longer degenerate and separated by 11–14 cm.$^{-1}$, perhaps as a result of the low site symmetry of the complex ion in the

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