TABLE I

| | | | | | | |
|---|---|---|---|---|---|---|
| Temp., °K. | 150 | 200 | 300 | 400 | 500 | 600 |
| Gram susceptibility $\times 10^6$ | 225 | 69.7 | 31.2 | 18.2 | 13.2 | 9.9 |
| Temp., °K. | 700 | 800 | 900 | 1000 | 1100 | |
| Gram susceptibility $\times 10^6$ | 8.2 | 6.71 | 5.75 | 4.87 | 4.36 | |

TABLE II

TRANSITION TEMPERATURES IN THE COBALT–SULFUR SYSTEM

| Transition | No. of observations | Transition temp., °K. This work | Hansen | Kuznetsov |
|---|---|---|---|---|
| $Co_9S_8$ decomposes | 8 | 1106 ± 3 | 1106, 1108 | 1103 |
| $Co_4S_3$ eutectoid | 3 | 1065 ± 5 | 1053 | 1058 |
| $Co_4S_3$ peritectic | 8 | 1206 ± 6 | 1203, 1205 | 1208 |
| $Co_1S_1$ eutectoid | 3 | 710 ± 10 | About 733 | 748 |
| $Co_3S_4$ decomposes | 4 | 914 ± 2 | About 898 | |

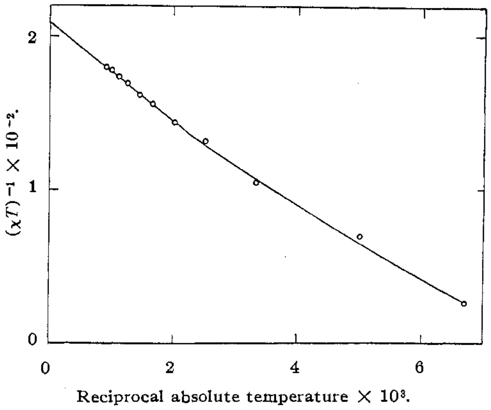

Figure 7.—Reciprocal of the product of gram susceptibility and absolute temperature for $CoS_2$ plotted as a function of reciprocal absolute temperature.

various temperatures, the susceptibility of the phase was calculated by extrapolation of isotherms similar to those in Figures 3 and 4 to the composition corresponding to $CoS_2$. The values obtained are listed in Table I.

Measurements in this composition region were made down to liquid nitrogen temperatures and the $CoS_2$ was found to be ferromagnetic with a Curie temperature of 116°K., in fair agreement with the 110°K. reported previously.[7]

In Figure 7, the reciprocal of the product of the gram susceptibility and the absolute temperature, $(\chi T)^{-1}$, is plotted against the reciprocal absolute temperature, $T^{-1}$. Danielian[17] has recently suggested that a graph of this kind is more advantageous than the usual $\chi^{-1}$ *vs.* $T$ plot for the determination of the Curie constant. The Curie constant, obtained as the reciprocal of the value of the intercept at $T^{-1}$ equal to zero, is 0.59 on a molar basis for $CoS_2$. The gram susceptibilities used in Figure 7 were corrected for the diamagnetic contributions of the constituent ions by the addition of $0.68 \times 10^{-6}$. The Curie constant gives a value of the magnetic moment of 2.17 B.M. compared with the 1.85 found by Néel and Benoit. This magnetic moment corresponds to that of one unpaired electron with a partially quenched orbital contribution.

From the linear portion of Figure 7 at high temperatures the Weiss constant is 153°. Néel and Benoit found 161° for the Weiss constant. The deviation from linearity observed at lower temperatures signals the breakdown of the model taking into account nearest neighbor interactions only.

**(B) Transition Temperatures.**—The various transition temperatures observed in this work, compared with values compiled by Hansen and those of Kuznetsov, are shown in Table II.

[17] A. Danielian, *Proc. Phys. Soc.* (London), **80**, 981 (1962).

---

CONTRIBUTION FROM THE CHEMISTRY DIVISION, RESEARCH DEPARTMENT,
U. S. NAVAL ORDNANCE TEST STATION, CHINA LAKE, CALIFORNIA

# Formation of a Monobromo Complex of Nickel(II) in 2-Methoxyethanol

BY DWIGHT A. FINE

*Received June 29, 1965*

The formation of a monobromo complex of nickel(II) in 2-methoxyethanol solution has been demonstrated by a spectrophotometric study. The absorption spectrum of the complex indicates that it is a solvated, octahedral species of the type $Ni(solv)_5Br^+$.

## Introduction

Studies of halide complexes of nickel(II) in organic solvents have shown that the formation of complexes with up to four coordinated halides can occur, the lower complexes being octahedral and the higher complexes tetrahedral. The higher, tetrahedral complexes have been well-characterized,[1-4] but the picture with respect to the lower complexes is still not clear.

A number of workers have obtained evidence for the possible formation of an octahedral monohalo complex of nickel(II) in organic solvents.[5-10] The situation is

---

[1] N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

[2] C. Furlani and G. Morpurgo, *Z. physik. Chem.*, **28**, 93 (1961).

[3] D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).

[4] D. A. Fine, *Inorg. Chem.*, **4**, 345 (1965).

[5] S. A. Shchukarev and O. A. Lobaneva, *Dokl. Akad. Nauk SSSR*, **105**, 741 (1955).

[6] M. Baaz, V. Gutmann, G. Hampel, and J. R. Masaguer, *Monatsh.*, **93**, 1416 (1962).

[7] H. Hubacek, B. Stančić, and V. Gutmann, *ibid.*, **94**, 1118 (1963).

[8] I. V. Nelson and R. T. Iwamoto, *J. Electroanal. Chem.*, **6**, 234 (1963).

[9] T. Šramko, *Chem. Zvesti*, **17**, 725 (1963).

[10] C. P. Nash and M. S. Jenkins, *J. Phys. Chem.*, **68**, 356 (1964).

often complicated by the simultaneous formation of other halide complexes. By the use of 2-methoxyethanol as a solvent, we have been able to demonstrate the formation of an octahedral monobromo complex of nickel(II) and to determine the absorption spectrum of the species in this solvent.

## Experimental Section

**Materials.**—Anhydrous nickelous bromide was prepared by allowing hydrobromic acid to react with nickelous carbonate (Baker analyzed reagent), evaporating the resulting solution to dryness, and drying the salt at 110°. Composition was checked by bromide analysis.

Tetraethylammonium bromide was Eastman Kodak salt, recrystallized from water and ethanol.

Silver perchlorate was G. F. Smith anhydrous $AgClO_4$.

2-Methoxyethanol was Matheson Coleman and Bell solvent (dielectric constant = 16.0). The solvent was dried over magnesium sulfate, redistilled, and passed through an alumina column.

Stock solutions of nickelous perchlorate in 2-methoxyethanol were prepared by the addition of solutions containing a stoichiometric equivalent of silver perchlorate to solutions of anhydrous nickelous bromide. The precipitated silver bromide was centrifuged out. The nickel concentration was checked by gravimetric analysis with dimethylglyoxime.

Stock solutions of tetraethylammonium perchlorate were prepared in a similar manner, by the addition of solutions of silver perchlorate to solutions of tetraethylammonium bromide.

**Measurements.**—Absorption spectra were measured on a Cary Model 14 recording spectrophotometer, Serial 244. The cell compartment was thermostated to 25.0 ± 0.2°. Matched quartz cells of 1-, 2-, and 5-cm. path length were employed.

Solutions for spectrophotometric measurement were prepared in volumetric flasks. Stock solutions of nickelous perchlorate were mixed with stock solutions of tetraethylammonium bromide (and in some cases tetraethylammonium perchlorate) and the resulting solution was diluted to the mark with solvent.

## Results

The addition of tetraethylammonium bromide to nickelous perchlorate in 2-methoxyethanol produces spectra in the visible and near-infrared regions which indicate a two-species equilibrium. The spectra show six isosbestic points; these points occur at ~360, 393, 550, 670, 955, and 1170 mμ. Each of the three principal bands of the uncomplexed (solvated) nickelous ion is shifted toward longer wave lengths; this shift is accompanied by an increase in intensity. At nickel concentrations between 0.01 and 0.05 *M*, this behavior persists up to a molar ratio of bromide to nickel of 5–10. Beyond this bromide concentration the spectrum is relatively insensitive to addition of bromide; the isosbestic points are eventually lost, but no conspicuous new peaks appear in the spectrum. The uncomplexed nickelous ion and the complex formed by the addition of bromide are apparently the only species present at significant concentrations at 25°. Visibly, the green color of the nickelous perchlorate solution changes to bright yellow-green as bromide is added. The absorbance values obtained at two different wave lengths for six series of solutions are shown in Table I.

TABLE I

ABSORBANCES OF SOLUTIONS OF $Ni(ClO_4)_2 + N(C_2H_5)_4Br$ IN 2-METHOXYETHANOL

| | Molar Ratio Br⁻/Ni | 780mμ | 430mμ | Molar Ratio Br⁻/Ni | 780mμ | 430mμ | Molar Ratio Br⁻/Ni | 780mμ | 430mμ |
|---|---|---|---|---|---|---|---|---|---|
| Ni | $4.80 \times 10^{-2}$ gr. atom $l^{-1}$ [c] | | | $1.34 \times 10^{-2}$ gr. atom $l^{-1}$ [d] | | | $2.98 \times 10^{-2}$ gr. atom $l^{-1}$ [b,c] | | |
| | 0 | 0.200 | 0.362 | 0 | 0.150 | 0.234 | 0 | 0.127 | 0.207 |
| | 0.35 | 0.314 | 0.758 | 0.50 | 0.255 | 0.608 | 0.50 | 0.207 | 0.596 |
| | 0.50 | 0.360 | 0.916 | 0.75 | 0.316 | 0.797 | 0.75 | 0.228 | 0.664 |
| | 0.75 | 0.432 | 1.128 | 1.0 | 0.346 | 0.904 | 1.0 | 0.267 | 0.794 |
| | 1.0 | 0.487 | 1.302 | 2.0 | 0.392 | 1.034 | 1.5 | 0.278 | 0.825 |
| | 2.0 | 0.548 | 1.503 | 3.0 | 0.402 | 1.064 | 2.0 | 0.316 | 0.986 |
| | 4.0 | 0.568 | 1.570 | 4.0 | 0.411 | 1.090 | 3.0 | 0.330 | 1.024 |
| | | | | 5.0 | 0.421 | 1.110 | 4.0 | 0.349 | 1.047 |
| Ni | $2.46 \times 10^{-2}$ gr. atom $l^{-1}$ [c] | | | $4.89 \times 10^{-2}$ gr. atom $l^{-1}$ [a,c] | | | $1.49 \times 10^{-2}$ gr. atom $l^{-1}$ [b,d] | | |
| | 0 | 0.110 | 0.170 | 0 | 0.195 | 0.322 | 0 | 0.069 | 0.105 |
| | 0.30 | 0.164 | 0.360 | 0.50 | 0.344 | 0.814 | 0.50 | 0.089 | 0.150 |
| | 0.50 | 0.188 | 0.449 | 0.75 | 0.412 | 1.022 | 1.0 | 0.117 | 0.302 |
| | 0.70 | 0.217 | 0.539 | 1.0 | 0.457 | 1.168 | 2.0 | 0.145 | 0.424 |
| | 1.0 | 0.248 | 0.640 | 1.5 | 0.509 | 1.349 | 4.0 | 0.167 | 0.460 |
| | 1.5 | 0.271 | 0.720 | 2.0 | 0.542 | 1.480 | 6.0 | 0.175 | 0.484 |
| | 2.0 | 0.290 | 0.780 | 3.0 | 0.564 | 1.532 | 8.0 | 0.184 | 0.494 |
| | 8.0 | 0.300 | 0.815 | | | | | | |

[a] Ionic strength kept at 0.25 by addition of $N(C_2H_5)_4ClO_4$. [b] Ionic strength kept at 0.15 by addition of $N(C_2H_5)_4ClO_4$. [c] 2-cm. cell. [d] 5-cm. cell.

The most likely situation is that a monobromo complex is formed, and the spectral data support this contention. If the spectrum formed at Br/Ni ratios of 5–10 is taken as an approximation to the spectrum of the complex, then the fraction of nickel in the form of the complex in solutions having lower Br/Ni ratios can be estimated as $f_c = (A - A_0)/(A_{\text{lim}} - A_0)$, where $A$ is the observed absorbance at a given wave length for the particular solution, $A_0$ is the absorbance of the uncomplexed $Ni^{2+}$, and $A_{\text{lim}}$ the absorbance for the "limiting" spectrum, *i.e.*, the spectrum formed at higher bromide concentrations. The free bromide concentration is then given by

$$(\text{Br}^-) = \Sigma\text{Br} - nf_c\Sigma\text{Ni} \qquad (1)$$

where ΣBr and ΣNi represent the total bromide and nickel concentrations and $n$ is the number of bromides coordinated to the nickel. This estimation was made using data for wave lengths at 10-mμ intervals between 800 and 680 and between 500 and 400 mμ. In all cases where Br/Ni was less than 2, $f_c$ turns out to be too large for $n$ to be greater than 1.

A second indication that $n$ equals 1 is obtained by application of the Rose–Drago equation[11] to the absorbance data. The expression for a 1:1 complex is, in the present case

$$\beta_1^{-1} = \frac{A - A_0}{\epsilon_c - \epsilon_{\text{Ni}^{2+}}} - \Sigma\text{Ni} - \Sigma\text{Br} + \Sigma\text{Ni}\Sigma\text{Br}\,\frac{\epsilon_c - \epsilon_{\text{Ni}^{2+}}}{A - A_0} \qquad (2)$$

where $\beta_1$ is the formation constant of the complex, and $\epsilon_c$ and $\epsilon_{\text{Ni}^{2+}}$ are the molar extinction coefficients of the complex and the uncomplexed $Ni^{2+}$ ion. The corresponding expression for a 2:1 complex is

$$\beta_2^{-1} = \frac{4(\Sigma\text{Ni} + \Sigma\text{Br})(A - A_0)}{(\epsilon_c - \epsilon_{\text{Ni}^{2+}})} - \frac{4(A - A_0)^2}{(\epsilon_c - \epsilon_{\text{Ni}^{2+}})} - 4\Sigma\text{Ni}\Sigma\text{Br} - \Sigma\text{Br}^2 + \frac{\Sigma\text{Ni}\Sigma\text{Br}^2(\epsilon_c - \epsilon_0)}{A - A_0} \qquad (3)$$

These expressions were applied to the absorbance data at 430 mμ, the wave length at which $A - A_0$ is a maximum. Values of $\epsilon_c - \epsilon_{\text{Ni}^{2+}}$ were obtained by solution of pairs of simultaneous equations. The average values of $\epsilon_c - \epsilon_{\text{Ni}^{2+}}$ obtained in this manner were then

---

(11) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).

TABLE II

VALUES OF $f_c$ CALCULATED FROM ABSORBANCES AND FROM EQ. 2, 3, AND 6; $\Sigma\text{Ni} = 4.80 \times 10^{-2}$, $\lambda = 430$

| $Br^-/Ni$ | $f_c$, abs.[a] | $f_c$, (2)[b] | $f_c$, (3)[c] | $f_1$, (6)[d] |
|---|---|---|---|---|
| 0.35 | 0.31 | 0.31 | 0.21 | 0.31 |
| 0.50 | 0.43 | 0.44 | 0.30 | 0.43 |
| 0.75 | 0.62 | 0.61 | 0.41 | 0.61 |
| 1.0 | 0.77 | 0.75 | 0.50 | 0.76 |
| 2.0 | 0.93 | 0.91 | 0.61 | 0.92 |
| 4.0 | 1.00 | 0.96 | 0.64 | 0.98 |

[a] Calculated from absorbance data. [b] Calculated for 1:1 complex, using eq. 2, with $\epsilon_c - \epsilon_{Ni^{2+}} = 13.1$. [c] Calculated for 2:1 complex, using eq. 3, with $\epsilon_c - \epsilon_{Ni^{2+}} = 19.5$. [d] Final values obtained from plots of $R/(\epsilon - \epsilon_c)$ *vs.* $R + 1 - f_1$.

TABLE III

EXAMPLES OF $(\epsilon_1 - \epsilon_0)$ VALUES OBTAINED FROM PLOTS OF $R/(\epsilon - \epsilon_0)$ *vs.* $R + 1 + f_1$

| | $\epsilon_1 - \epsilon_0$ | | | |
|---|---|---|---|---|
| $\lambda$, m$\mu$ | I[a] | II | III | IV |
| 800 | 3.6 | 3.5 | 3.6 | 3.2 |
| 780 | 4.1 | 3.9 | 4.0 | 4.1 |
| 750 | 2.8 | 2.9 | 2.8 | 3.0 |
| 710 | 2.1 | 2.2 | 2.1 | 2.3 |
| 430 | 12.2 | 13.5 | 13.1 | 14.1 |
| 410 | 8.1 | 7.4 | 7.5 | 7.2 |

[a] $\Sigma$Ni: I, 0.0480; II, 0.0246; III, 0.0134; IV, 0.0489.

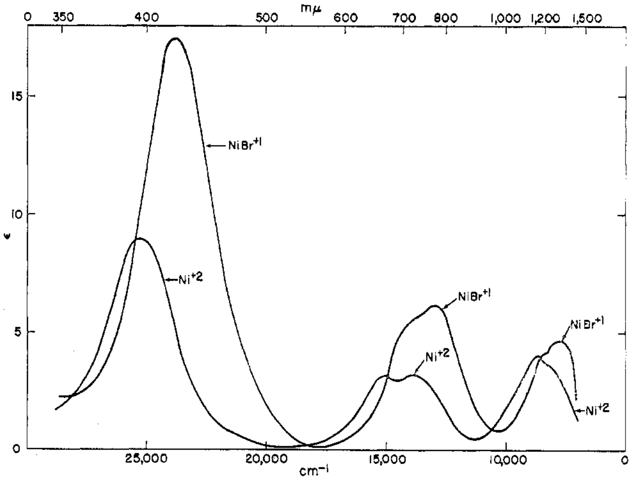

Figure 1.—Absorption spectra of nickelous and monobromonickelate ions in 2-methoxyethanol.

used to calculate $f_c$ from the relationship $f_c = (\epsilon - \epsilon_{Ni^{2+}})/(\epsilon_c - \epsilon_{Ni^{2+}})$. The values of $f_c$ thus obtained can then be used to calculate values of the free bromide concentration from eq. 1. Again, it was found that the calculated values of $f_c$ for solutions where Br/Ni was less than 2 were too large for $n$ to be greater than 1. The values of $f_c$ obtained in this manner for one series of solutions are shown in Table II, along with the values estimated as described previously.

The most likely nature of the complex having been established, one could apply eq. 2 to the absorbance data at different wave lengths. It proved more convenient, however, to treat the data by a method similar to one used by Bale, Davies, and Monk.[12] If the equilibrium is between uncomplexed $Ni^{2+}$ and a monobromo complex $NiBr^+$, then the formation quotient $\beta_1$ for the complex is given by

$$\beta_1 = \frac{f_1}{(1 - f_1)\Sigma\text{Ni}(R - f_1)} \tag{4}$$

where $f_1$ stands for the fraction of the total nickel in the form of the complex, and $R$ for the molar ratio of bromide to nickel. If we represent the molar extinction coefficients of the uncomplexed species and the complex by $\epsilon_0$ and $\epsilon_1$, respectively, and the extinction coefficient of a mixture of the two species by $\epsilon$, we have

$$f_1 = \frac{\epsilon - \epsilon_0}{\epsilon_1 - \epsilon_0} \tag{5}$$

Combination of (4) and (5) leads to the relationship

$$\frac{R}{\epsilon - \epsilon_0} = \frac{R + 1 - f_1}{\epsilon_1 - \epsilon_0} + \frac{1}{\beta_1 \Sigma\text{Ni}(\epsilon_1 - \epsilon_0)} \tag{6}$$

Hence a plot of $R/(\epsilon - \epsilon_0)$ *vs.* $R + 1 - f_1$ should yield a straight line with a slope equal to $(\epsilon_1 - \epsilon_0)^{-1}$. Since $\epsilon_0$ is known, the plot permits the determination of $\epsilon_1$ at the selected wave length. The procedure employed was to estimate values of $f_1$, as described previously, and plot $R/(\epsilon - \epsilon_0)$ *vs.* $R + 1 - f_1$ to obtain a first value of $\epsilon_1 - \epsilon_0$. This value was used to calculate a new set of $f_1$ values, and the process was repeated until constant values of $f_1$ and $\epsilon_1 - \epsilon_0$ were obtained. Data from four different sets of solutions were treated in this manner; nickel concentration in the solutions ranged from 0.0134 to 0.0489 $M$. Spectra produced by molar ratios of bromide to nickel between 0 and 4 were utilized for the plots. Plots were made for wave lengths at 10-m$\mu$ intervals between 690 and 800 m$\mu$ and between 390 and 500 m$\mu$. The plots were linear, and convergence of $f_1$ values was usually obtained after three plots. In most cases, the final value of $f_1$ did not differ by more than 0.03 from the first estimate. The $f_1$ values obtained for $\Sigma\text{Ni} = 4.80 \times 10^{-2}$ and $\lambda = 430$ are shown in Table II, along with the values obtained by previous calculations. Examples of $\epsilon_1 - \epsilon_0$ values obtained from the plots are shown in Table III. The spectrum derived in this manner was quite close to the spectrum observed at molar ratios of bromide to nickel between 5 and 10. Thus the results of this treatment of the spectral data substantiate the assumption that the complex formed is $NiBr^+$.

The spectrum of the uncomplexed $Ni^{2+}$ and the spectrum of the monobromo complex $NiBr^+$ are shown in Figure 1. In the case of $NiBr^+$, the extinction coefficients in the regions 690–800 and 390–500 m$\mu$ are the average values obtained from the plots of $R/(\epsilon - \epsilon_0)$ *vs.* $R + 1 - f_1$; the spectrum in the remainder of the region shown was obtained from the absorbances produced at Br/Ni ratios between 5 and 10.

The spectral data do not permit an accurate determination of the formation quotient $\beta_1$. It will be shown that $\beta_1$ is extremely sensitive to errors in $f_1$; also, lack of information on activity coefficients in 2-methoxyethanol prevents an evaluation of the true formation constant. An estimate of the quotient is possible, however. In

---

(12) W. D. Bale, E. W. Davies, and C. B. Monk, *Trans. Faraday Soc.*, **52**, 816 (1956).

TABLE IV

VALUES OF FORMATION QUOTIENT $\beta_1$ OBTAINED FOR SOLUTIONS OF $Ni(ClO_4)_2 + N(C_2H_5)_4Br + N(C_2H_5)_4ClO_4$

| I. $\Sigma Ni = 0.0489$, $\mu = 0.25$ | | II. $\Sigma Ni = 0.0298$, $\mu = 0.15$ | | III. $\Sigma Ni = 0.0149$, $\mu = 0.15$ | |
|---|---|---|---|---|---|
| $Br^-/Ni$ | $\beta_1 \times 10^{-2}$ | $Br^-/Ni$ | $\beta_1 \times 10^{-2}$ | $Br^-/Ni$ | $\beta_1 \times 10^{-2}$ |
| 0.50 | 0.93 | 0.50 | 0.97 | 0.50 | 0.46 |
| 0.75 | 1.1 | 0.75 | 0.86 | 1.0 | 0.63 |
| 1.0 | 1.1 | 1.0 | 1.1 | 2.0 | 0.68 |
| 1.5 | 1.0 | 1.5 | 0.70 | 4.0 | 0.66 |
| 2.0 | 1.2 | 2.0 | 1.1 | 6.0 | 0.57 |
| 3.0 | 1.0 | 3.0 | 0.96 | | |
| | 1.0 ± 0.1[a] | | 0.94 ± 0.1[a] | | 0.67 ± 0.1[a] |

[a] Obtained from plots of log $(f_1/(1 - f_1))$ *vs.* log $\Sigma Ni(R - f_1)$; other values calculated from eq. 4.

order to make the estimate more meaningful, additional sets of solutions were prepared in which the ionic strength was held approximately constant by the addition of tetraethylammonium perchlorate. Spectra were taken and data were plotted in the manner described above; absorbance values are shown in Table I. The final values of $f_1$ obtained from the plots were used to construct a plot of log $(f_1/(1 - f_1))$ *vs.* log $\Sigma Ni(R - f_1)$; this yields a straight line having a slope of 1.0 and an intercept equal to $\beta_1$. The values of $\beta_1$ obtained in this manner are shown in Table IV, along with values calculated by use of eq. 4 (direct application of eq. 2 or 6 involves taking differences between nearly equal quantities and does not lead to accurate results). The values obtained indicate that the formation quotient of the monobromo complex falls in the range $(0.9 \pm 0.3) \times 10^2$ at 25°, at an ionic strength of 0.15–0.25. The data obtained for the solutions in which no $N(C_2H_5)_4ClO_4$ was added indicate a formation quotient of the same order of magnitude as the $\beta_1$ obtained for the solutions containing the salt, but higher by a factor of 2–5; the estimated range of ionic strength in these solutions is 0.03–0.15. The values of $\epsilon_1 - \epsilon_0$ for the solutions containing $N(C_2H_5)_4ClO_4$ agreed quite well with those obtained in the absence of the salt. The addition of neutral salt shifts the equilibrium toward the uncomplexed species; similar behavior has been observed in acetone solution with higher bromide complexes of nickel(II).[4]

The variations and uncertainties in $\beta_1$ might seem at first glance to cast doubt upon the reliability of the $\epsilon_1$ values. There are several considerations, however, which indicate that these values are trustworthy. The accuracy of both $\beta_1$ and $\epsilon_1$ depends ultimately upon the accuracy of $f_1$, as shown by eq. 4 and 5. The $f_1$ values cannot be expected to be more accurate than ±0.02. The probable error in $\beta_1$ is given approximately by

$$\Delta\beta_1 = \frac{\sigma\beta_1}{\sigma f_1}\Delta f_1 = \frac{R - f_1^2}{\Sigma Ni(1 - f_1)^2(R - f_1)^2}\Delta f_1 \quad (7)$$

where $\Delta f_1$ is the probable error in $f_1$; similarly, the probable error in $\epsilon_1$ is given by

$$\Delta\epsilon_1 = \frac{\partial\epsilon_1}{\partial f_1}\Delta f_1 = \frac{-(\epsilon - \epsilon_0)}{f_1^2}\Delta f_1 \quad (8)$$

Computation of these quantities, taking $\Delta f_1$ as ±0.02, shows that the probable error in $\epsilon_1$ is much smaller than the corresponding probable error in $\beta_1$. Results for two cases are shown in Table V. It is seen that errors of 30% in $\beta_1$ correspond to errors of less than 3% in $\epsilon_1$; furthermore, data which produce a change of a factor of 2 in $\beta_1$ produce no significant change in the $\epsilon_1$ values. Other indications of the reliability of the $\epsilon_1$ values are the close agreement of the derived spectrum with the spectrum observed at higher bromide concentrations, the agreement between the $\epsilon_1$ values obtained from different series of solutions, and the good agreement of the $f_1$ values obtained from eq. 2 and 6 with the values estimated from the absorbances as described previously; in the latter case, the method of estimation does not assume any constancy of equilibrium quotient.

TABLE V

EXAMPLES OF CALCULATED VALUES AND PROBABLE ERRORS OF $\beta_1$ AND $\epsilon_1 - \epsilon_0$

I. $\Sigma Ni = 4.80 \times 10^{-2}$

| $R$ | $f_1$ | $\beta_1 \times 10^{-2}$ | $\epsilon_1 - \epsilon_0$, 780 mμ | $\epsilon_1 - \epsilon_0$, 430 mμ |
|---|---|---|---|---|
| 0.35 | 0.31 | 2.4 ± 1.4 | 3.8 ± 0.2 | 13.3 ± 0.9 |
| 0.50 | 0.43 | 2.2 ± 0.8 | 3.9 ± 0.2 | 13.4 ± 0.6 |
| 0.75 | 0.61 | 2.3 ± 0.6 | 4.0 ± 0.1 | 13.1 ± 0.4 |
| 1.0 | 0.76 | 2.7 ± 0.6 | 3.9 ± 0.1 | 12.9 ± 0.3 |
| 2.0 | 0.92 | 2.2 ± 0.7 | 3.9 ± 0.1 | 12.9 ± 0.3 |
| 4.0 | 0.98 | 3.4 ± 3.6 | 3.9 ± 0.1 | 12.9 ± 0.3 |

II. $\Sigma Ni = 4.89 \times 10^{-2}$, $\mu = 0.25$

| $R$ | $f_1$ | $\beta_1 \times 10^{-2}$ | $\epsilon_1 - \epsilon_0$, 780 mμ | $\epsilon_1 - \epsilon_0$, 430 mμ |
|---|---|---|---|---|
| 0.60 | 0.37 | 0.9 ± 0.2 | 4.0 ± 0.2 | 13.5 ± 0.8 |
| 0.75 | 0.54 | 1.1 ± 0.2 | 4.1 ± 0.2 | 13.3 ± 0.5 |
| 1.0 | 0.66 | 1.1 ± 0.2 | 4.1 ± 0.1 | 13.0 ± 0.4 |
| 1.5 | 0.80 | 1.0 ± 0.2 | 4.0 ± 0.1 | 13.1 ± 0.3 |
| 2.0 | 0.89 | 1.2 ± 0.3 | 3.9 ± 0.1 | 13.3 ± 0.3 |
| 3.0 | 0.93 | 1.0 ± 0.4 | 4.1 ± 0.1 | 13.3 ± 0.3 |

## Discussion

The spectral parameters of the two nickel species are presented in Table VI. The positions of the three absorption bands are estimated from the center of gravity of each band. The positions and intensities of the bands indicate that both species are octahedral; the $\nu_1$ band is due to the transition $^3A_{2g} \rightarrow {}^3T_{2g}$, the $\nu_2$ band to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and the $\nu_3$ band to $^3A_{2g} \rightarrow {}^3T_{1g}(P)$.[13] The $\nu_1$ bands indicate $Dq$ values of about 860 and 810 for the two species. The position of the $\nu_2$ band can be calculated from $Dq$ and the observed position of the $\nu_3$ band[13,14]; the close agreement between the calculated and the observed positions provides further confirmation of the octahedral structure of the two

TABLE VI

ELECTRONIC SPECTRA OF $Ni^{+2}$ AND $NiBr^+$ IN 2-METHOXYETHANOL

| | $Ni^{+2}$ | | | | $NiBr^+$ | | | |
|---|---|---|---|---|---|---|---|---|
| $\lambda_{max}$, mμ | 1160 | 730 | 664 | 396 | 1270 | 775 | 710 | 421 |
| $\epsilon_{max}$, l./mole cm. | 4.1 | 3.3 | 3.2 | 9.0 | 4.7 | 6.2 | 5.4 sh[a] | 17.4 |
| $\nu_1$, cm.$^{-1}$ | 8,600 | | | | 8,100 | | | |
| $\nu_2$, cm.$^{-1}$ | 14,300 | | | | 13,400 | | | |
| $\nu_3$, cm.$^{-1}$ | 25,300 | | | | 23,700 | | | |
| $\nu_2$, calcd., cm.$^{-1}$ | 14,270 | | | | 13,430 | | | |

[a] sh = shoulder.

---

(13) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **6**, 134 (1959).

(14) V. Imhof and R. S. Drago, *Inorg. Chem.*, **4**, 427 (1965).

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.

[15] C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).
[16] R. T. Pflaum and A. J. Popov, *Anal. chim. Acta*, **13**, 165 (1955).
[17] W. Schneider, *Helv. chim. Acta*, **46**, 1842 (1963).
[18] R. S. Drago, D. W. Meek, M. D. Joesten, and L. La Roche, *Inorg. Chem.*, **2**, 124 (1963).
[19] R. S. Drago, D. W. Meek, R. Longhi, and M. D. Joesten, *ibid.*, **2**, 1056 (1963).
[20] R. F. Pasternack and R. A. Plane, *ibid.*, **4**, 1171 (1965).
[21] N. S. Chhonkar, *J. Chem. Phys.*, **41**, 3683 (1964).
[22] L. I. Katzin, *ibid.*, **36**, 3034 (1962).
[23] A. Kiss and P. Csokán, *Z. anorg. allgem. Chem.*, **245**, 2355 (1941).
[24] R. H. Herber and J. W. Irvine, *J. Am. Chem. Soc.*, **78**, 905 (1956).
[25] K. B. Yatsimirskii and V. D. Korableva, *Izv. VUZ, Khim.*, **19**, No. 4 (1958).
[26] D. A. Netzel and H. A. Droll, *Inorg. Chem.*, **2**, 412 (1963).

---

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

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

BY DEAN C. LUEHRS, REYNOLD T. IWAMOTO, AND JACOB KLEINBERG

*Received August 30, 1965*

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

---

[1] J. Kratohvil and B. Težak, *Rec. trav. chim.*, **75**, 774 (1956).
[2] L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.
[3] I. M. Kolthoff and T. B. Reddy, *J. Electrochem. Soc.*, **108**, 980 (1961).