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Mixed-Ligand Complexes of Nickel(II) with Bromide and Chloride in Acetonitrile[1a]

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Received December 30, 1969

The constants for the formation of mixed-ligand complexes of nickel(II) with bromide and chloride in acetonitrile have been measured. They are $\log \dagger K_1 = 2.05 \pm 0.08$ for $NiBr_4^{2-} + Cl^- = NiBr_3Cl^{2-} + Br^-$, $\log \dagger K_2 = 1.68 \pm 0.09$ for $NiBr_3Cl^{2-} + Cl^- = NiBr_2Cl_2^{2-} + Br^-$, $\log \dagger K_3 = 1.78 \pm 0.08$ for $NiBr_2Cl_2^{2-} + Cl^- = NiBrCl_3^{2-} + Br^-$, and $\log \dagger K_4 = 1.79 \pm 0.06$ for $NiBrCl_3^{2-} + Cl^- = NiCl_4^{2-} + Br^-$. Tetraethylammonium halides were employed to adjust the total halide concentration to 0.35 *M* and also maintain the ionic strength at that value. Contrary to most previous studies dealing with mixed-ligand complexes, these complexes with nickel are formed in less than statistical amounts. The ratio of the formation constants for $NiCl_4^{2-}$ and $NiBr_4^{2-}$ is calculated as $\log (\beta_{4Cl}/\beta_{4Br}) = 7.30 \pm 0.08$. This is a clear indication that nickel(II) is a class a or hard acceptor with respect to the halides as donors in acetonitrile solvent. The stepwise formation of the tetracoordinated halide complex was measured as $\log K_{4Cl} = 3.05$ for $NiCl_3^- + Cl^- = NiCl_4^{2-}$ and $\log K_{4Br} = 1.80$ for $NiBr_3^- + Br^- = NiBr_4^{2-}$.

In recent years there has been considerable interest in the halide complexes of nickel in nonaqueous systems. Through the interpretation of the absorption spectra exhibited by nickel under different ligand field environments it has been shown that the nickel in many of these solvents exists in a tetrahedral configuration.[2-8] This has been shown to be the case when acetonitrile is the solvent.[3,4,8] Although much work has been done on the theoretical interpretation of the spectra of these halide complexes, virtually nothing has been done on their equilibria in solution.

Mixed-halide complexes of nickel are known to exist, and the compound $[(C_2H_5)_4N]_2NiCl_2Br_2$ has been prepared in the solid state.[4] The purpose of this paper is to study the degree to which the mixed complexes form in acetonitrile and to measure their formation constants. The methods used for the analysis of the spectrophotometric data and the advantages of the approach have been described in previous publications.[9,10]

Experimental Section

Apparatus.—Absorption spectra were recorded with a Cary Model 14 spectrophotometer. Silica absorption cells of 1- and 10-cm path lengths were used which had fused-on glass reservoirs of 100–150-ml capacities. The cell openings were sealed with rubber serum bottle caps so that titrant solutions could be added from a syringe microburet (Micro-Metric Instruments, Model SB2) without exposure to atmospheric moisture. The serum caps were boiled under reflux with acetonitrile for several days before use to remove an extractable impurity which caused difficulty in the ultraviolet measurements. Even with this treatment, measurements could not be made with reliability at less than 340 mμ. The rubber itself did not swell or suffer any deterioration on contact with acetonitrile. All measurements were made at room temperature which was recorded before and after each titration and was always found to be 25 ± 0.5°.

Materials. Acetonitrile.—Fisher Certified grade acetonitrile was stored over silica gel from 1 to 4 weeks with intermittent shaking. It was distilled from calcium hydride through a 20-plate Oldershaw sieve fractionating column, the first and last 10% fractions being rejected. This treatment should completely free the solvent of acetic acid and water, the most worrisome impurities for this study.[11] The solvent was dispensed by siphoning from a storage bottle protected with a drying tube, and it came into contact with glass and Teflon only.

Bis(tetraethylammonium) Tetrabromonickelate(II) and Bis(tetraethylammonium) Tetrachloronickelate(II).—These compounds were precipitated from ethanol according to the method of Gill and Nyholm.[5] The salts were recrystallized from acetonitrile and dried under vacuum at 45°. *Anal.* Calcd for $[(C_2H_5)_4N]_2NiBr_4$: Ni, 9.19. Found: Ni, 9.13. The standard nickel solutions in acetonitrile were prepared by direct weighing of these salts.

Tetraethylammonium Bromide and Tetraethylammonium Chloride.—Eastman White Label grade salts were recrystallized from chloroform and vacuum dried.

Tetrabutylammonium Perchlorate.—This salt was precipitated from aqueous solution by mixing tetrabutylammonium bromide and sodium perchlorate. It was recrystallized by dissolving in a minimum of hot acetone and then precipitated by adding water. It was dried at 60° *in vacuo*, and an aqueous–acetone solution gave no bromide precipitate when tested with silver nitrate.

Results

General Equations for the Determination of the Equilibrium Constants.

—All of the equilibria studied may be classed as belonging to the two types

$$NiX_4 + Y = NiX_3Y + X \qquad \text{(type I)}$$

$$NiX_3Y + Y = NiX_2Y_2 + X \qquad \text{(type II)}$$

Charges are omitted to simplify subsequent equations. A definition of the meanings of the moieties X and Y

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[2] (a) L. I. Katzin, *Nature*, **182**, 1013 (1958); (b) *J. Chem. Phys.*, **36**, 3034 (1962).

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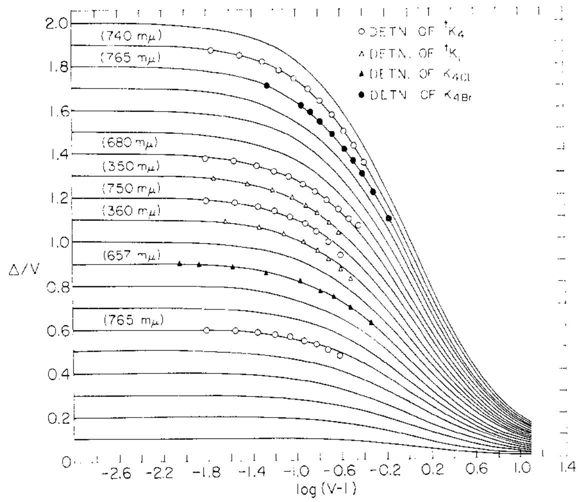

Figure 1.—The family of normalized curves: $\Delta/V = A - A_3$; $\log (V - 1) = \log K + \log R$. Some typical plots of A *vs.* $\log R$ at various wavelengths shown fitted onto appropriate curves.

determines the equilibrium being studied along with its associated equilibrium constant. It is convenient also to define the ratio of the free concentrations of Y and X as an additional variable R; thus, $R = [\mathrm{Y}]/[\mathrm{X}]$. If A is the measured absorbance, and A_4, A_3, and A_2 are the absorbances if all of the nickel were present as the respective species NiX_4, NiX_3Y, and NiX_2Y_2, then it follows that

$$A = \frac{A_4 + A_3KR}{1 + KR} \tag{1}$$

for solutions in which only the single equilibrium of type I is of importance, and free Y and X are in all cases nonabsorbing species. The constant, K, is the equilibrium constant of the type I reaction. The absorbances are read from the recorded absorption spectra at various wavelengths. The data were then treated by the normalized-curve method of Srivastava and Newman.[9] The difference between the absorption efficiencies of the two forms participating in the equilibrium at the wavelength in question is defined as $\Delta = A_4 - A_3$. Substituting this into eq 1 gives

$$\Delta(1 + KR)^{-1} = A - A_3 \tag{2}$$

Defining the auxiliary variable V as

$$V = 1 + KR \tag{3}$$

or, in logarithmic form

$$\log (V - 1) = \log K + \log R \tag{4}$$

eq 2 becomes

$$\Delta/V = A - A_3 \tag{5}$$

The data are plotted as A *vs.* $\log R$ (or, as $-A$ *vs.* $\log R$, depending on whether the absorbance increases or decreases with increasing $\log R$), and the points are fitted to the family of curves Δ/V *vs.* $\log (V - 1)$. The curve which gives the best fit yields $\log K = -\log R$ at the point where $\log (V - 1) = 0$. The value of A_4 can be read directly from the fitted curve, and the value of A_3 can be obtained from $\Delta = A_4 - A_3$ using the value of Δ of the curve for which the best fit was obtained. Figure 1 shows the family of curves and some of the data which were fitted.

The following equation holds for solutions in which both the first and second replacement steps are of importance

$$A = \frac{A_4 + A_3KR + A_2KK^*R^2}{1 + KR + KK^*R^2} \tag{6}$$

The constant K^* is the equilibrium constant of the type II reaction. This equation can be rearranged to

$$\frac{(A - A_2)R^2}{(A_4 - A)} = (KK^*)^{-1} + \frac{(A_3 - A)\,R}{(A_4 - A)\,K^*} \tag{7}$$

The data were treated by plotting the left-hand term of eq 7 against $R(A_3 - A)/(A_4 - A)$ for various assumed values of A_2. A straight line should be obtained only when the proper value of A_2 is selected. Actually, in these instances the plots were quite insensitive to the value of A_2 chosen as is seen in Figure 2. The slope of the plot is seen to be $1/K^*$ and the intercept is $1/KK^*$. The meanings of the terms of eq 1 and 6 for the various equilibria and species which were studied are summarized in Table I.

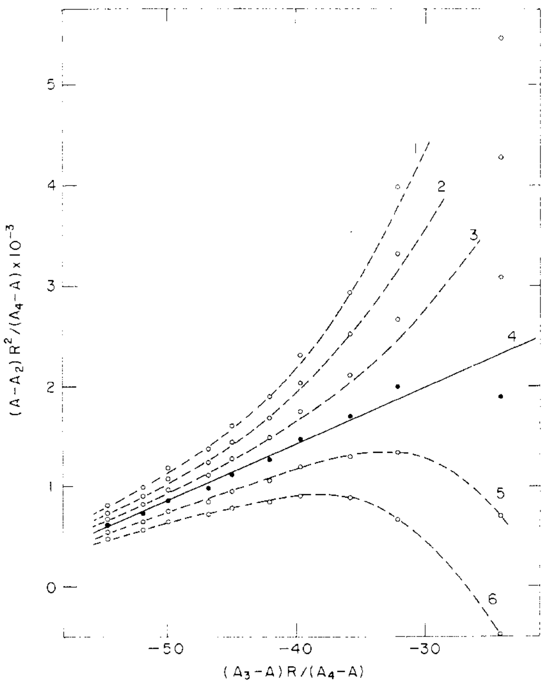

Figure 2.—A typical plot for the determination of the constant for the reaction $NiX_3Y + Y = NiX_2Y_2 + X$. Determination of the formation constant for $NiBrCl_3^{2-} + Br^- = NiBr_2Cl_2^{2-} + Cl^-$ at 750 mμ. Curve numbers and their various assumed values of A_2 are: 1, 1.8; 2, 1.7; 3, 1.6; 4, 1.5; 5, 1.4; 6, 1.3.

Determination of the Stepwise Formation Constants of the Tetracoordinated Halide Complexes.—In the study of mixed-ligand complex formation it is important that coordination saturation of the complexes be maintained. For this reason, the equilibrium constants $K_{4\mathrm{Cl}}$ and $K_{4\mathrm{Br}}$ in Table I were measured.

TABLE I

NOTATION AND LIST OF EQUILIBRIA STUDIED

Equilibrium[a]	Equilibrium constant
$NiCl_3L^- + Cl^- = NiCl_4^{2-} + L$	K_{4Cl}
$NiBr_3L^- + Br^- = NiBr_4^{2-} + L$	K_{4Br}
$NiBr_{5-n}Cl_{n-1}^{2-} + Cl^- = NiBr_{4-n}Cl_n^{2-} + Br^-$	$\dagger K_n$

X	Y	R	K	K^*	A_4	A_3	A_2
Br^-	Cl^-	$[Cl^-]/[Br^-]$	$\dagger K_1$	$\dagger K_2$	$NiBr_4^{2-}$	$NiBr_3Cl^{2-}$	$NiBr_2Cl_2^{2-}$
Cl^-	Br^-	$[Br^-]/[Cl^-]$	$1/\dagger K_4$	$1/\dagger K_3$	$NiCl_4^{2-}$	$NiCl_3Br^{2-}$	$NiBr_2Cl_2^{2-}$
Cl^-	L	$1/[Cl^-]$	$1/K_{4Cl}$		$NiCl_4^{2-}$	$NiCl_3L^{2-}$	
Br^-	L	$1/[Br^-]$	$1/K_{4Br}$		$NiBr_4^{2-}$	$NiBr_3L^-$	

[a] L = acetonitrile.

Samples of $((C_2H_5)_4N)_2NiCl_4$ and $((C_2H_5)_4N)_2NiBr_4$ were weighed out and dissolved in acetonitrile. Equal aliquots of the chloride salt solution were added to $(C_2H_5)_4NCl$ (solution 1) and $(C_4H_9)_4NClO_4$ (solution 2) for the chloride experiments and equal aliquots of the bromide salt solution were added to $(C_2H_5)_4NBr$ (solution 3) and $(C_4H_9)_4NClO_4$ (solution 4) for the bromide experiments. Solution 2 was titrated with solution 1, and solution 4 with solution 3. In this manner the total nickel concentration was maintained constant during the titrations (for the chloride experiment, $C_{Ni} = 8.70 \times 10^{-3}$ *M;* for the bromide, $C_{Ni} = 6.97 \times 10^{-3}$ *M*) and the ionic medium was maintained constant with the $(C_4H_9)_4NClO_4$ (0.249 *M* for the chloride titration; 0.304 *M* for the bromide titration) while the halide concentration was varied. In each case 10-ml volumes of the perchlorate solutions were titrated with the halide solutions in reservoir cells of 1-cm path length. The spectral characteristics observed for the limiting species compare favorably with previously reported values and are shown in Table II.

TABLE II

SPECTRAL CHARACTERISTICS OF $NiCl_4^{2-}$ AND $NiBr_4^{2-}$

Isosbestic points, mμ	λ_{max}, mμ	ϵ_{max}, mμ	Ref
	$NiCl_4^{2-}$		
	657	202	. . .
	656	204[a]	4
	657	196	3
629, 512	703	209	. . .
	702	210[a]	4
	705	202	3
	$NiBr_4^{2-}$		
	708	281	. . .
	704	271[a]	4
	707	250[b]	3
	709	259[c]	8
659, ~550	756	279	. . .
	754	267[a]	4
	756	241[b]	3
	758	263[c]	8

[a] In nitromethane as solvent. The authors report that the values in acetonitrile are 2–3% higher than these, but they are not actually cited. [b] These values are believed to be too low because insufficient excess bromide was added to prevent dissociation completely. [c] These values are estimated graphically from Figure 5 of ref 8. They are, however, suspect because of the presence of chloride in the system.

The appearance of isosbestic points in each of the systems indicates that an equilibrium between two species is involved. The spectral characteristics suggest that the equilibrium is between tetrahedrally coordinated nickel species which in one case, for example, would be $NiCl_4^{2-}$ and $NiCl_3L^-$, where L represents coordinated solvent.[3,8]

In each experiment the free concentration of halide, $[Cl^-]$ or $[Br^-]$, was first approximated by using the total halide concentration of the system. An approximate value of K_4 was then found as described above. This value was used to compute the free halide concentration from an equation derived from material balances on the system and the expression for K_4. For the chloride experiment this equation is

$$K_{4Cl}[Cl^-]^2 + [K_{4Cl}(4C_{Ni} - C_{Cl}) + 1][Cl^-] - C_{Cl} + 3C_{Ni} = 0 \quad (8)$$

where C_{Ni} and C_{Cl} represent the total analytical concentration of nickel and chloride present in the solutions being measured. The calculation was repeated until consistent values of K_4 were obtained. Two or three cycles were sufficient in all cases. The values of K_4 found at each wavelength were then averaged and the results follow: $\log K_{4Cl} = 3.05$ (ionic strength 0.249 *M*); $\log K_{4Br} = 1.80$ (ionic strength 0.304 *M*).

These constants show that the tetrabromo complex is much more dissociated in acetonitrile than is the tetrachloro complex. The free bromide concentration is limited by the solubility of tetraethylammonium bromide in acetonitrile (*ca.* 0.35 *M*), and it is seen that even at the highest possible bromide concentrations about 5% of the nickel may exist in the form of the $NiBr_3L^-$ species.

Determination of the Stepwise Formation Constants of the Mixed Complexes.—The ionic medium chosen for the study of the formation constants of the mixed complexes was selected to correspond to nearly saturated solutions of tetraethylammonium bromide in acetonitrile. Since the analogous chloride is more soluble, it was possible to prepare solutions for spectrophotometry which had a constant total halide concentration but varying ratios of bromide to chloride. By keeping the halide concentration high, the only equilibria which need to be considered are those involving the coordinatively saturated complexes. These are the equilibria represented by $\dagger K_1$ through $\dagger K_4$ in Table I.

Figure 3 shows the visible absorption spectra of the parent complexes $NiBr_4^{2-}$ and $NiCl_4^{2-}$ (corresponding to curves 1 and 21, respectively) as well as some of the spectra obtained at intermediate ratios of bromide to chloride. It is apparent that mixed complexes are being formed, since no combination of the parent spectra could produce the intermediate curves. The values of R, where R in this figure is the ratio of $[Br^-]$ to $[Cl^-]$, cited for the individual curves clearly indicate that the formation of the chloro complexes is very much favored over that of the bromo complexes.

Values of R were first approximated from the total halide concentrations of the solutions. As described earlier for type I reactions, the values of the first approximations of K were then found. These were used to recalculate the R values from eq 9 which is readily

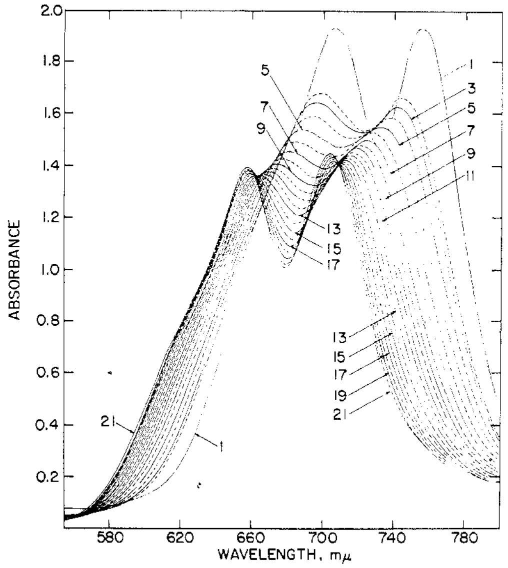

Figure 3.—Absorption spectra of a solution of $[(C_2H_4)_4N]_2NiBr_4$ to which increasing amounts of chloride have been added. The total concentration of nickel and the total halide concentration are constant at 6.92×10^{-4} *M* and 0.343 *M*, respectively; 10-cm cells. The values of $R = [Br^-]/[Cl^-]$ for some of the curves are: 5, 121; 7, 55.7; 9, 33.3; 11, 22.5; 13, 15.0; 15, 9.28; 17, 5.43; 19, 2.81; 21, 0.976.

derived from the expression for *K* and appropriate material balances for the system. Two or three such

$$(C_X - 3C_{Ni})R^2 + [C_{Ni} - C_Y + (C_X - 4C_{Ni})K^{-1}]R - C_YK^{-1} = 0 \quad (9)$$

cycles generally resulted in consistent *R* values. The values of *K* obtained at different wavelengths were averaged and the results are shown in Table III.

TABLE III

VALUES OF THE CONSTANTS FOR THE STEPWISE REPLACEMENT REACTIONS[a]

	Log $\dagger K_1$	Log $\dagger K_1\dagger K_2$	Log $\dagger K_2$	Log $\dagger K_4$	Log $\dagger K_3\dagger K_4$	Log $\dagger K_3$
	2.00 (350)	3.70 (350)		1.80 (630)	3.45 (690)	
	2.05 (355)	3.67 (355)		1.80 (730)	3.58 (750)	
	2.10 (360)	3.82 (360)		1.75 (740)	3.68 (765)	
				1.80 (750)		
Av	2.05 ± 0.08	3.73 ± 0.08	1.68 ± 0.09	1.79 ± 0.06	3.57 ± 0.08	1.78 ± 0.08

[a] Wavelengths (mμ) at which the constants were measured are given in parentheses. Uncertainties in the constants were estimated at the 90% confidence level assuming the standard deviation of a single measurement to be 0.05 log unit.

It is evident that this procedure of successive approximations would not be necessary if C_{Ni} could be made sufficiently small so that the *R* values could be calculated directly from the ratios of C_Y to C_X. Within the limits imposed by the solubility of tetraethylammonium bromide, the practical limit of 10 cm for the cell path length, and the molar absorptivities of the complexes, this was not possible. In fact, because the first bromide in $NiBr_4^{2-}$ is displaced so readily by chloride, it was not found possible to determine $\dagger K_1$ from data taken in the visible region (see Figure 3) and reliable *R* values could not be obtained. For this reason, data in the ultraviolet region were taken where the nickel concentration could be reduced from 6.92×10^{-4} to 5.90×10^{-5} *M* (see Figure 4).

After determining $\dagger K_1$ and $\dagger K_4$, the constants of the second replacement reactions, $\dagger K_2$ and $\dagger K_3$, were found as described earlier. The *R* values were first calculated from eq 9 using the $\dagger K_1$ or $\dagger K_4$ value just determined. Preliminary values of $\dagger K_2$ or $\dagger K_3$ were obtained and the values of *R* were corrected for the formation of the NiX_2Y_2 complex. This was done by solving equations of the following type using successive approximations

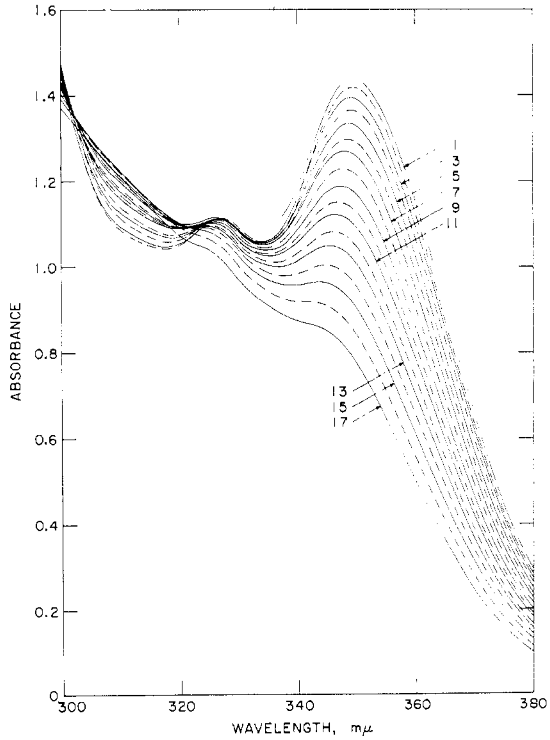

Figure 4.—Ultraviolet absorption spectra of a solution of $[(C_2H_4)_4N]_2NiBr_4$ to which increasing amounts of chloride have been added. The total concentration of nickel and the total halide concentration are constant at 5.90×10^{-5} *M* and 0.340 *M*, respectively; 10-cm cells. The values of $R = [Br^-]/[Cl^-]$ for some of the curves are: 3, 2720; 5, 1090; 7, 651; 9, 417; 11, 307; 13, 235; 15, 176; 17, 106.

$$R = \frac{C_{Cl} - (2\dagger K_1\dagger K_2R^2 + 3\dagger K_1R + 4)C_{Ni}J}{C_{Br} - (2\dagger K_2R + 1)\dagger K_1RC_{Ni}J} \quad (10)$$

where $J = (1 + \dagger K_1R + \dagger K_1\dagger K_2R^2)^{-1}$. The second refinement of the *R* values resulted in only relatively small changes in *R*. They were perhaps unnecessary considering the rather large uncertainties in determining the constants of the second replacement reactions. The values found for $\dagger K_2$ and $\dagger K_3$ are given in Table III.

Measurements Made at the Isosbestic Point.—The presence of an isosbestic point at 689.5 mμ in the spectra of Figure 3 provides an independent means for the determination of the product $\dagger K_3 \dagger K_4$ through the direct use of the normalized curves, Δ/V *vs.* log $(V - 1)$. At this wavelength the molar absorptivities of $NiCl_4^{2-}$ and $NiCl_3Br^{2-}$ are equal and are consequently indistinguishable spectrophotometrically. If A_0 represents the absorbance of the solution when all the nickel is present either as $NiCl_4^{2-}$ or as $NiCl_3Br^{2-}$ and A_2 is the absorbance when all the nickel is present as $NiCl_2Br_2^{2-}$, then it may be derived that

$$A = \frac{A_0 + (A_0R/\dagger K_4) + (A_2R^2/\dagger K_3 \dagger K_4)}{1 + (R/\dagger K_4) + (R^2/\dagger K_3 \dagger K_4)} \qquad (11)$$

If V is defined as

$$V = \frac{1 + (R/\dagger K_4) + (R^2/\dagger K_3 \dagger K_4)}{1 + (R/\dagger K_4)} \qquad (12)$$

then in logarithmic form

$$\log (V - 1) = 2 \log R - \log \dagger K_3 \dagger K_4 - \log [1 + (R/\dagger K_4)] \qquad (13)$$

and defining $\Delta = A_0 - A_2$, eq 11 becomes

$$\Delta/V = A - A_2 \qquad (14)$$

A plot of $-A$ *vs.* 2 log R − log $[1 + (R/\dagger K_4)]$ can be fitted to the normalized curves previously employed but now yields log $\dagger K_3 \dagger K_4 = 2 \log R - \log [1 + (R/\dagger K_4)]$ at the point where log $(V - 1) = 0$. The previously determined value of $\dagger K_4 = 63$ was used to construct the plot, and the value of log $\dagger K_3 \dagger K_4$ which resulted is shown in Table III and is in good agreement with values obtained by the conventional technique.

Derived Formation Constants.—The constants for the formation of the three mixed species from the parent reactants may be calculated by appropriate combinations of $\dagger K_1$ through $\dagger K_4$. The values derived are shown in Table IV along with the constants expected if there is purely statistical mixing of the ligands.[12]

TABLE IV
OBSERVED AND STATISTICAL VALUES OF THE FORMATION CONSTANTS

Reaction	Log *K* Found[a]	Log *K* Statistical
$^3/_4NiCl_4^{2-} + ^1/_4NiBr_4^{2-} = NiCl_3Br^{2-}$	0.035 ± 0.09	0.60
$^1/_2NiCl_4^{2-} + ^1/_2NiBr_4^{2-} = NiCl_2Br_2^{2-}$	0.080 ± 0.09	0.78
$^1/_4NiCl_4^{2-} + ^3/_4NiBr_4^{2-} = NiClBr_3^{2-}$	0.225 ± 0.10	0.60

[a] Uncertainties in the derived constants were calculated at the 90% confidence level with the same assumption used for the values in Table III.

The fractional distribution of the complexes as a function of the halide ratio is shown in Figure 5. Because the mixed species are formed in relatively small concentration regardless of the halide ratio, resolution of the experimental spectra into the spectra of the individual species was not successful.

The relative stabilities of $NiCl_4^{2-}$ and $NiBr_4^{2-}$ can be obtained by summing $\dagger K_1$ through $\dagger K_4$ from which

$$\frac{\beta_{4Cl}}{\beta_{4Br}} = 10^{7.30 \pm 0.08} = \frac{(NiCl_4^{2-})(Br^-)^4}{(NiBr_4^{2-})(Cl^-)^4} \qquad (15)$$

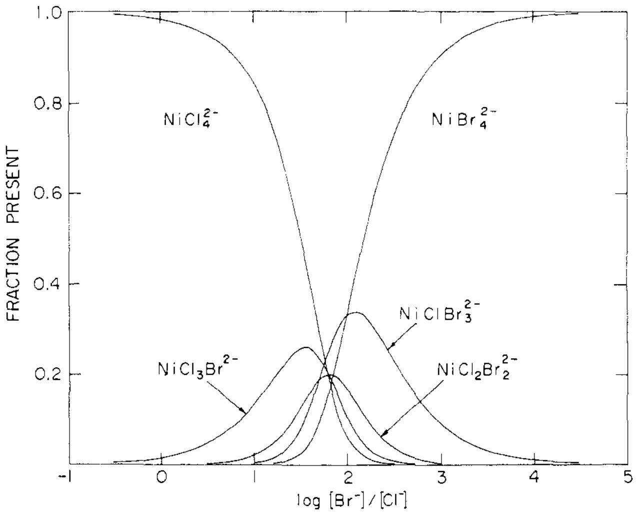

Figure 5.—Fractional distribution of complexes as a function of the halide ratio. The total halide concentration is 0.34 *M*.

Discussion

The unusual behavior of the formation of less than statistical amounts of the mixed complexes cannot be fully explained at present. We have shown that Ni(II) is clearly a class a or hard acceptor with respect to the halides as donors in acetonitrile solvent. The stability sequence expected is therefore $F^- \gg Cl^- > Br^- > I^-$. Data from aqueous media have shown that the fluoride complexes of Ni(II) are more stable than the chlorides.[13] The present study shows that overall the chloride system is more than seven orders of magnitude more stable than the bromide in acetonitrile. The iodides were found to be so unstable as to make the study of mixed bromide–iodide complexes untenable in this solvent. In a previous investigation,[14] with dimethyl sulfone as the solvent, it was found that the chloride stability was approximately one order of magnitude less than the bromide but that the bromide was more than two orders greater than the iodide. It is quite remarkable that there is a difference of more than eight orders of magnitude for the relative chloride and bromide stabilities in these two solvents. The position of nickel in the periodic table does not allow it to be clearly placed with either halide stability sequence.[15,16] An overriding consideration would appear to be the nature of the solvent and its interplay with steric hindrance in the formation of the tetrahalonickelate(II) ions.

Ahrland has pointed out that the character of an acceptor varies with the properties of the donor and he stated as a general rule: "The more polarizable the donor, the more pronounced the b character of a certain acceptor."[17] One might expect on this basis that as the more tightly held chlorides are replaced by the more polarizable bromides to form the mixed species, the nature of the nickel acceptor acquires more b character.

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Since this is an effect working against the normal a character of the acceptor, the stabilities of the parent complexes $NiCl_4^{2-}$ and $NiBr_4^{2-}$ may be regarded as being brought relatively closer together and the mixed complexes consequently form in less than statistical amounts.

Stabilization of mixed complexes may also be regarded similarly. For example, when chloride is replaced by bromide on a clearly b type acceptor such as Pd(II), marked stabilization of the mixed species is observed.[9] Whether this is due solely to the induction of more b character to the Pd(II) as bromides are added, or, putting it another way, the factors considered in the polarized ion model of Marcus and Eliezer[18,19] are operating exclusively, cannot be determined. It is believed that these considerations are not adequate to cover all cases because the role of solvation in the formation of mixed complexes has been largely ignored in most studies. Generally, investigations are carried out in aqueous media with the almost universal conclusion that the mixed species are stabilized relative to their statistically expected formation. The suggestion has been made that this stabilization is due at least in part to greater hydration of the less symmetrical mixed complexes.[20] Polarographic data show that solvation of the simple Ni(II) ion is much greater by water than it is by acetonitrile.[21] There is thus no reason to expect the solvents to behave similarly. Just how distortions from tetrahedral configurations and uniform charge distribution may affect the stabilization or destabilization of the mixed complexes is difficult to assess.

In a recent series of papers Griffiths and Scarrow[22] have proposed that the tetrahedral nickel tetrahalide complexes are stabilized by ion-pair formation in acetone as solvent and to a lesser extent in dimethyl sulfone. The difference in behavior in the two solvents was interpreted as being due to the difference in dielectric constants (acetone, 20.7; dimethyl sulfone, 40). Stabilization of the divalent anions, NiX_4^{2-}, in these solvents was shown to decrease with increasing cation size clearly suggesting the formation of ion pairs. Some ion-pair formation should therefore also occur in acetonitrile ($D = 36.2$). If the chloro complexes are progressively stabilized in this manner as their size decreases, then less than statistical distribution of the ligands can result. For example, if $\log K_1$ is taken to be 2.05 as found, then a statistical distribution of the ligands would give the following values for the other constants: $\log K_2 = 1.624$; $\log K_3 = 1.272$; $\log K_4 = 0.846$. The value of $\log K_4$ was observed to be 1.79. If the complexes are considered to be progressively stabilized in going from $NiBr_3Cl^{2-}$ to $NiCl_4^{2-}$, then estimates of the other constants might be $\log K_1 = 2.05$, $\log K_2 = 1.939$, $\log K_3 = 1.902$, and $\log K_4 = 1.79$. These values lead to the following formation constants of the mixed species from the parent complexes: for $NiBr_3Cl^{2-}$, $\log K = 0.130$; for $NiBr_2Cl_2^{2-}$, $\log K = 0.149$; for $NiBrCl_3^{2-}$, $\log K = 0.130$. These values are seen to be far less than the statistical values (Table IV). Thus, preferential ion pairing of the progressively smaller chloride species seems to be the most reasonable explanation of the abnormal distribution of complexes observed.

The apparent instability of the chloride complexes in dimethyl sulfone previously reported[14] as compared to this work is probably also due to differences in ion pairing since lithium salts were used to provide the halide ions. Griffiths and Scarrow[22] have shown that lithium salts are the least effective of the many salts used to promote the formation of nickel tetrahalide complexes.

Another factor of importance in the relative stabilities of mixed complexes is the nature of the ligands. The cyanide ion, for example, shows a marked reluctance to enter into mixed complexes. Several examples are known where no mixed species whatever are formed,[23,24] and two, where less than statistical formation is observed.[25,26] Other than the present work, the only example of mixed-halide complexes which form in less than statistical amounts is the complexes formed from the interaction of $BiCl_3$ with BiI_3 in dioxane as solvent.[27] Clearly, a definitive explanation of unusually low formation constants of mixed complexes awaits the accumulation of data on more systems.

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