

# Effects of Cations upon Absorption Spectra

## Part 3.—The Interaction of Chloride and Nickel(II) in Acetone and Dimethyl Sulphone.\*

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The various equilibria which occur when nickel(II) in acetone and dimethyl sulphone reacts with the chloride ion are examined. Various species containing solvent and chloride are detected spectrophotometrically and the role of the added cations in particular is explored. These cations affect the relative concentrations of the various species involved in specific ways.

The interaction of chloride ions and nickel(II) has been investigated in a wide variety of solvents and a brief survey has been given.<sup>1</sup> Studies in acetone have not, however, been reported. This paper is concerned chiefly with the effects of the added cations upon the equilibria observed and the identification of the intermediate species obtained in the conversion of octahedral hexasolvated nickel(II) to tetrahedral tetrachloronickelate(II) in acetone and dimethyl sulphone. The presence of the tetrachloro complex has been established in the latter solvent<sup>2</sup> using excess chloride but the formation of intermediate species has not previously been studied. It is fortunate that the visible spectra of octa- and tetrahedral nickel(II) complexes are easily distinguishable. The transitions studied in detail are the  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  transition for the octahedral complexes and the  ${}^3T_1(F) \rightarrow {}^3T_1(P)$  for the tetrahedral complexes.

## EXPERIMENTAL

### MATERIALS

All chemicals were of the highest grade of purity available. The preparation of anhydrous  $\text{Ni}(\text{ClO}_4)_2$  has been given in part 1<sup>1</sup> and of tetramethylammonium chloride in part 2.<sup>3</sup> Anhydrous  $\text{NiCl}_2$  was kindly donated by Mr. G. Brumfitt of the Department of Physical Chemistry, University of Leeds. Lithium chloride was heated at  $250^\circ\text{C}$  for several hours and stored in a desiccator until required. Tetraethylammonium chloride was recrystallized from acetone and dried and stored under vacuum. Tetraphenylarsonium chloride and Hyamine 10X (benzyltrimethyl-2-{2-[4-(1,3,3-tetramethylbutyl)-*m*-tolyl]oxy}ethoxy} ethylammonium chloride monohydrate), kindly donated by Lennig Chemicals Ltd., were used without further purification.

Tri-*n*-butylbenzylphosphonium chloride was prepared by addition of tri-*n*-butylphosphine (0.5 M) to benzyl chloride (0.63 M) in methyl ethyl ketone (100 ml). The mixture was refluxed at  $80^\circ\text{C}$  for 5 h under oxygen-free nitrogen and the precipitate that separated out on cooling was recrystallized twice from benzene after first removing the solvent and excess benzyl chloride under vacuum at room temperature. The product was dried under vacuum

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at 60°C and the yield was 80 % of the theoretical, m.p. 164-5°C. The chloride content was determined by Volhard's method, using nitrobenzene to coagulate the silver chloride: found 10.75 %, calculated 10.80 %.

The purification of the solvent acetone has been given earlier<sup>1</sup> and dimethyl sulphone was recrystallized twice from water + ethanol mixtures and sublimed under reduced pressure, m.p. 110°C.

#### SPECTRAL MEASUREMENTS

Details of the spectrophotometers used have been given.<sup>1</sup> The furnace used for the dimethyl sulphone studies and the temperature controlling and measuring devices have also been described.<sup>3</sup> Spectra were measured from 400 to 800 nm.

#### PREPARATION OF SOLUTIONS

**ACETONE.**—LiCl, and in particular NiCl<sub>2</sub>, are not very soluble in acetone. Ni(ClO<sub>4</sub>)<sub>2</sub> is much more soluble and, within experimental error, no spectral differences could be detected between experiments employing either nickel salt. The perchlorate was therefore normally used. To obtain various Cl/Ni mole ratios, stock solutions of LiCl and Ni(ClO<sub>4</sub>)<sub>2</sub> were prepared and, using a microburette, known volumes of each solution were added to volumetric flasks, which were then made up to the mark with acetone. Care was taken to ensure that the solubility product of NiCl<sub>2</sub> was never exceeded. The maximum concentration of any chloride or nickel(II) in any solution did not exceed 10<sup>-2</sup> M. Each solution in an experimental run contained the same concentration of nickel so that spectra could be compared directly. 4 or 10 cm path length cells were generally used. All solutions were tightly stoppered and care was taken to ensure that the pick-up of atmospheric moisture was minimal. The addition of water up to 1 % by volume produced no observable effects upon the measured spectra.

**DIMETHYL SULPHONE.**—Pure crystals were weighed directly into the cell described in part 2<sup>3</sup> and the cell was placed in the furnace and thermostatted at 120°C. The volume of solvent used was calculated from the density of the melt.<sup>2</sup> A weighed portion of Ni(ClO<sub>4</sub>)<sub>2</sub> was dissolved in the melt and small weighed quantities of the selected chloride added, the spectrum being measured after each addition. The concentration of nickel(II) being constant during a run, the spectra were therefore directly comparable, but certain irregularities were found with powdery chlorides due to slow dissolution and to particles adhering to the sides of the cell. When this occurred the following procedure was adopted. Known weights of the chloride and dimethyl sulphone were added to the cell at room temperature and the mixture heated until molten. Weighed portions of Ni(ClO<sub>4</sub>)<sub>2</sub>, which dissolved rapidly, were added successively to the solution and the spectrum measured after each addition: the spectra were not now directly comparable. The maximum amount of Ni(ClO<sub>4</sub>)<sub>2</sub> ever added was 10 mg; no indication of a possible detonation was ever observed. The maximum concentration of perchlorate or chloride in any melt was around 5 × 10<sup>-2</sup> M. A slight positive pressure of dry oxygen-free nitrogen was maintained over each solution.

### RESULTS AND DISCUSSION

#### ACETONE SOLUTIONS

##### THE CHLORO-NICKEL COMPLEXES

Species such as [M(solvent)<sub>6</sub>]<sup>2+</sup>, [MX(solvent)<sub>5</sub>]<sup>+</sup>, [MX<sub>2</sub>(solvent)<sub>4</sub>]<sup>0</sup>, [MX<sub>2</sub>(solvent)<sub>2</sub>]<sup>0</sup>, [MX<sub>3</sub>(solvent)]<sup>-</sup>, and [MX<sub>4</sub>]<sup>2-</sup> have been reported in the extensive literature<sup>2, 4-12</sup> on nickel(II) in relatively weak coordinating solvents. Acetone is a moderately weak donor towards transition metal cations<sup>11</sup> but to date the various chloro-nickel complexes in acetone have not been established. We have found all of the above complexes in acetone except [NiCl<sub>2</sub>(solvent)<sub>2</sub>]<sup>0</sup>. We now establish these species with a minimum reference to standard arguments and note their spectral characteristics, which are later used in identifying the various equilibria.

HEXASOLVATED COMPLEX  $\text{NiS}_6^{2+}$ 

S represents an acetone molecule. A solution of nickel perchlorate in acetone exhibits an absorption band in the visible region attributed to the transition  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  (fig. 1) of the hexasolvated nickel ion,<sup>12</sup> the arrangement of acetone molecules around nickel being octahedral and the coordination through oxygen.<sup>12, 13</sup>

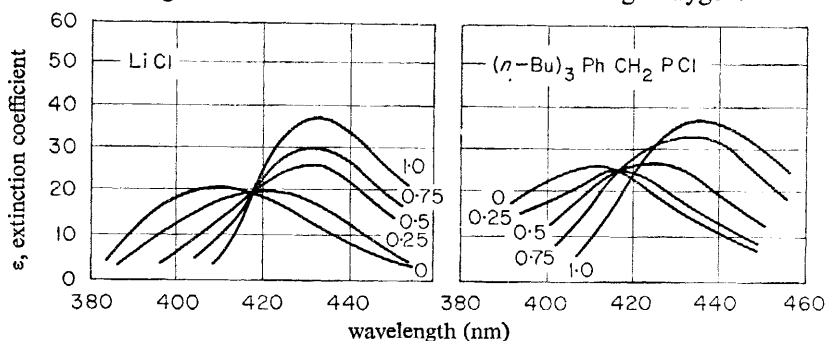


FIG. 1.—The effect of added chloride upon the  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  transition of hexasolvated nickel(II) in acetone up to a mole ratio of unity.

MONOCHLORO COMPLEX  $\text{NiClS}_5^+$ 

The spectrochemical behaviour of acetone is between that of chloride and water.<sup>14</sup> Unlike water in the aquonickel complex, acetone is readily replaced by many other ligands,<sup>1, 6, 7</sup> but the ligand field stabilization energy provided by water in hexa-aquanickel is only slightly greater than that provided by acetone ligands.<sup>12</sup> Replacement of water by chloride shifts the  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  transition to lower energies and increases its intensity.<sup>15</sup> When  $\text{NiCl}(\text{H}_2\text{O})_5^+$  is formed<sup>16</sup> the shift is around  $1\,000\text{ cm}^{-1}$  with an almost two-fold increase in molar extinction coefficient. The spectrum in fig. 1 at a Cl/Ni ratio of unity shows a similar shift and increase and is therefore reasonably identified with that of the species  $\text{NiClS}_5^+$ , with a basically octahedral structure but a  $C_{4v}$  point group.

DICHLORO COMPLEX  $\text{NiCl}_2\text{S}_4$ 

Replacement of a second acetone molecule by chloride results in a further shift and increase in extinction coefficient. The absorption maximum was expected in the 460 nm region<sup>15</sup> but its precise location could not be determined due to the concurrent presence of other species which have some absorption in this region in all the solutions examined. While the possibility of further substitution cannot be discounted we consider that when an absorption maximum is observed in this region it is most reasonably associated with the octahedral dichloro complex. Hexa-coordinated complexes of transition metals in which four of the ligands are acetone molecules have been established<sup>9, 12</sup> and the complexes  $[\text{NiX}_3(\text{solvent})_3]^-$  and  $[\text{NiX}_4(\text{solvent})_2]^{2-}$  have not yet been identified.

The dichloro complex can be formed as the cis isomer or the trans isomer. There is some evidence that trans substitutions occur<sup>12</sup> but subsequent rearrangement to give a cis complex could take place if this was the more thermodynamically stable.

TRICHLORO COMPLEX  $\text{NiCl}_3\text{S}^-$ 

From ligand field theory<sup>17</sup> this mixed ligand complex, having a structure based on tetrahedral symmetry but with point group  $C_{3v}$ , would be expected to have a band

system shifted slightly from that of the tetrahedral tetra-chloro complex  $\text{NiCl}_4^{2-}$ . Fine <sup>6</sup> has established that, with lithium bromide, at a Br/Ni ratio of 3 in acetone, the absorption spectrum is essentially that of  $\text{NiBr}_3\text{S}^-$ . We have confirmed this using other bromides <sup>1</sup> but fig. 2 shows that, at a Cl/Ni ratio of 3, identical spectra are not obtained with different chlorides. The observed spectrum, using lithium chloride, has absorption maxima which are close to those reported for  $[\text{NiCl}_3(\text{solvent})]^-$  in various solvents. (Table 1 contains these data, together with the band positions of  $\text{NiCl}_4^{2-}$  in various solvents.) Thus, this spectrum is attributed to  $\text{NiCl}_3\text{S}^-$  and the presence of this species in solution can readily be detected by its distinctive feature, a band and shoulder in the 620-625 and 580 nm regions respectively.

TABLE 1.—ABSORPTION MAXIMA IN THE VISIBLE REGION AND MOLAR EXTINCTION COEFFICIENTS FOR  $[\text{NiCl}_3(\text{solvent})]^-$  AND  $\text{NiCl}_4^{2-}$  IN VARIOUS SOLVENTS

solvent	peak positions in nm ( $\epsilon$ , molar extinction coefficients)						ref
	[NiCl <sub>3</sub> (solvent)] <sup>-</sup>			NiCl <sub>4</sub> <sup>2-</sup>			
acetone	580 (sh)	627	705	657.5 (192)	704.7 (193)		<i>a</i>
dimethyl sulphone	580 (sh)	627	705	652.2 (183)	705.3 (183)		<i>a</i>
				644.8 (155)	706.3 (148)		2
nitromethane				660.0 (167)	700.0 (167)		18, 19
				660.2 (204)	702.3 (210)		4
				660.2 (190)	710.5 (197)		10
dimethylformamide				660.2 (115)	699.3 (115)		4
				655.0	694.0		8
dimethylacetamide	572 (sh)	628 (155)	700 (sh)				20
acetonitrile	572 (sh)	615 (150)	700 (sh)	657.5 (160)	702.5 (160)		20
				660.2 (209)	702.3 (215)		4
				657.1 (196)	705.4 (202)		10
trimethylphosphate	580 (sh)	623 (135)	700 (80)	660 (100)	700 (120)		18
tri-n-butylphosphate	580 (sh)	627 (86)	698 (50)				21
ethanol		635	703	656 (204)	702 (210)		4
	sh = shoulder			<i>a</i> = this work			

sh = shoulder      *a* = this work

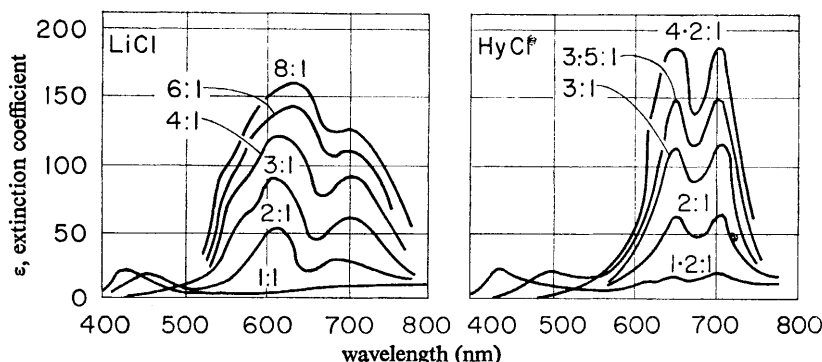


FIG. 2.—Increase in concentration of tetrahedral nickel(II) complexes with increasing Cl/Ni mol ratio.

#### TETRACHLORO COMPLEX $\text{NiCl}_4^{2-}$

The  ${}^3T_1(F) \rightarrow {}^3T_1(P)$  transition of this tetrahedral complex was obtained in acetone solutions containing an excess of all the chlorides investigated except lithium (fig. 2

and 3) and the absorption maxima and molar extinction coefficients agree closely with those reported in table 1 in other solvents. The band shapes are all essentially identical.

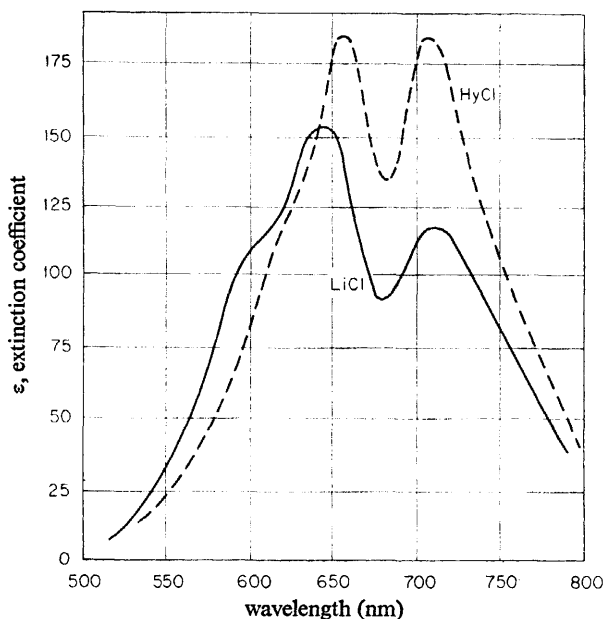
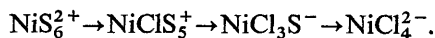


FIG. 3.—Spectra obtained at the highest Cl/Ni mol ratio obtainable in acetone in LiCl and HyCl.

#### EFFECTS OF CATIONS UPON THE EQUILIBRIA

The colour changes which occurred as various chlorides were added to acetone solutions of nickel(II) were from green to yellow, through olive-green to steel blue and finally to bright blue. The spectra were not temperature sensitive. Three chlorides were investigated in detail, lithium chloride, tri-*n*-butylbenzylphosphonium chloride and Hyamine 10X, this latter containing a long chain cation. From an examination of our spectra we propose that reasonable concentrations of the following species occur as increasing amounts of these three chloride sources are added to nickel perchlorate in acetone.

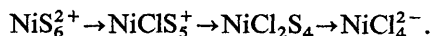
With LiCl,



With  $(\text{C}_4\text{H}_9)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{PCl}$ ,



With Hyamine 10X,



With all the chlorides used, their addition to nickel perchlorate resulted first in the formation of the monochloro species. The isosbestic point in fig. 1 at 417 nm suggests that only the monochloro and the hexasolvated species are initially present. When the isosbestic point is no longer observed then the dichloro species is also being formed; fig. 1 shows that this happens with the phosphonium chloride before all the

hexasolvated species has been converted into the monochloro species. A similar observation was made with Hyamine 10X. It was also noted that, with lithium chloride, the octahedral transition did not shift as much to lower energies as it did with the phosphonium chloride at comparable Cl/Ni ratios and that it fell more rapidly in intensity. We therefore conclude that, in the presence of lithium chloride, only a very small concentration of the dichloro complex is formed.

Fig. 2 shows that, with lithium chloride and Cl/Ni ratios of 3 and greater, the predominant species in solution is  $\text{NiCl}_3\text{S}^-$ , but with Hyamine 10X there is practically no evidence for this species; the spectrum is essentially that of  $\text{NiCl}_4^{2-}$ . Fig. 3 shows the spectra obtained in nearly saturated chloride solutions. The spectrum obtained with Hyamine 10X could be superimposed, within experimental error, upon the spectrum of  $\text{NiCl}_4^{2-}$  in regular tetrahedral symmetry.<sup>2</sup> The band at 640 nm with lithium chloride arises from approximately equal contributions from the 625 nm band of the trichloro complex and the 657 nm band of  $\text{NiCl}_4^{2-}$ .

The mole ratio plot (fig. 4), taken at the absorption maximum of the band of higher energy of the  $\text{NiCl}_4^{2-}$  species, demonstrates that, with Hyamine 10X, there is no discontinuity at a ratio of around 3 and hence no trichloro complex is formed with this chloride. Further, all the nickel in solution has been converted into  $\text{NiCl}_4^{2-}$  at a ratio of 4.2. With the phosphonium chloride, however, some  $\text{NiCl}_3\text{S}^-$  is detected but again almost all of the nickel is in the form  $\text{NiCl}_4^{2-}$  at a ratio of just over 4. It was also found, with this chloride, that the trichloro complex and  $\text{NiCl}_4^{2-}$  were present in solution in approximately equal concentration when the Cl/Ni ratio was between 1.53 and 2.22. With Hyamine 10X the 625 nm band of the trichloro complex can just be detected at a ratio of 1.2 (fig. 2).

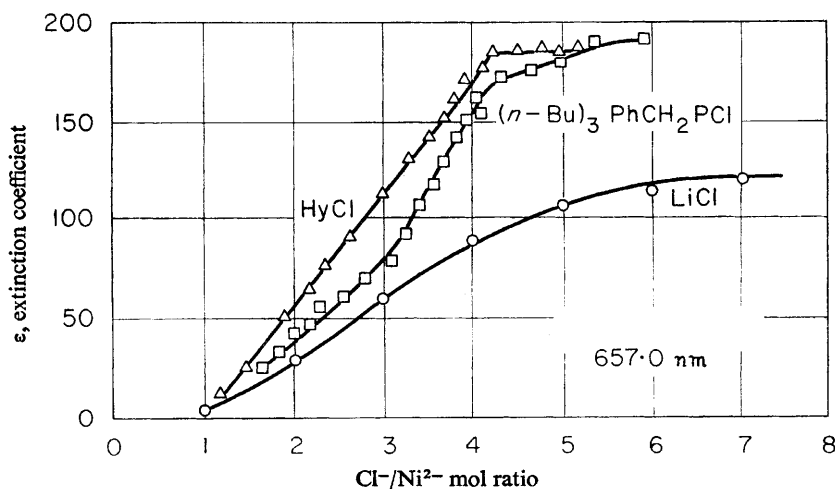


FIG.—4. Mol ratio plot at 657.0 nm with various chlorides in acetone.

With all the chlorides examined the equilibria were such that at no time were there only the species  $\text{NiCl}_3\text{S}^-$  and  $\text{NiCl}_4^{2-}$  in solution. This situation has been found in trimethylphosphate<sup>22</sup> and an isosbestic point was observed at 646 nm; we did not observe an isosbestic point in this region in any of our solutions. We have, however, obtained this equilibrium, and an isosbestic point, in acetone with the bromo and iodo complexes of nickel.<sup>1</sup>

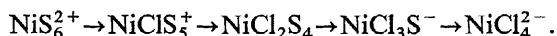


The current lithium chloride results are consistent with the earlier interpretation<sup>1</sup> of the lithium bromide and iodide data. Savedoff<sup>23</sup> has found that lithium chloride in acetone is mainly in the form of contact ion pairs. We have postulated<sup>1</sup> that the concentration of  $\text{NiBr}_4^{2-}$  in solution is proportional to the concentration of the bromide solvent shared ion-pairs present and that  $\text{NiBr}_4^{2-}$  is stabilized in solution by the formation of the species  $[\text{NiBr}_4(\text{acetone})\text{Li}]^-$ . Hence, at the highest Cl/Ni ratio obtainable there are not sufficient lithium chloride solvent shared ion-pairs for all of the nickel to be stabilized as the tetrachloro complex (fig. 3). The species identified in the presence of the phosphonium chloride are identical with those found for the bromo complexes.<sup>24</sup>

## DIMETHYL SULPHONE SOLUTIONS

### CHLORO-NICKEL COMPLEXES

The existence of  $\text{NiX}_4^{2-}$ , where X = Cl, Br or I, in regular tetrahedral symmetry has been established spectrophotometrically in dimethyl sulphone in the presence of excess lithium halide.<sup>2</sup> We have investigated the formation of  $\text{NiCl}_4^{2-}$  with several chlorides up to a Cl/Ni ratio of 50. The spectra obtained were similar to those observed with the phosphonium chloride in acetone and the following species were identified in solution:



S now represents dimethyl sulphone. The spectra were temperature independent.

The hexasolvated species has an absorption band at 420 nm. Addition of chloride caused this band to shift to around 480 nm before it disappeared, and this shift is consistent with the replacement of two sulphone ligands by two chloride ions. The presence of the trichloro species was again established by the appearance of an absorption at around 625 nm. Using lithium chloride it was apparent at Cl/Ni ratios between 2.13 and 3.04; with tetramethylammonium chloride at ratios between 1.94 and 2.88. The absorption maxima for the twin peaks of the  ${}^3T_1(F) \rightarrow {}^3T_1(P)$  transition of  $\text{NiCl}_4^{2-}$  obtained at high Cl/Ni ratios, and the spectral profile, agree well with the previous work.<sup>2</sup> We estimate that at a Cl/Ni ratio of 4.0 about 85 % of the nickel present is in the form  $\text{NiCl}_4^{2-}$ ; complete conversion to this complex is only achieved, however, at very high Cl/Ni ratios.

### EFFECTS OF CATIONS UPON THE EQUILIBRIA

In dimethyl sulphone the same chloro-nickel species given above were observed with each chloride, but the concentration of each species was not identical at identical Cl/Ni ratios. Certain cation effects are illustrated in the mole ratio plot (fig. 5) taken at 653 nm, the absorption maximum of one of the bands of  $\text{NiCl}_4^{2-}$  in dimethyl sulphone.

Although the trichloro complex is soon converted into the tetrachloro complex, it was observed that when the lithium cation is present the trichloro complex appears in slightly greater concentration than when the tetramethyl-ammonium cation is present. Also, it can still be detected at certain Cl/Ni ratios with lithium when it is no longer evident with tetramethylammonium chloride.

Fig. 5 shows that the effect of the cations upon the formation of the tetrachloro complex is  $(\text{CH}_3)_4\text{N}^+ > (\text{C}_2\text{H}_5)_4\text{N}^+ > \text{Hy}^+ > (\text{C}_4\text{H}_9)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{P}^+ > (\text{C}_6\text{H}_5)_4\text{As}^+ > \text{Li}^+$ . A similar plot at 625 nm, an absorption maximum of the trichloro species, with Cl/Ni ratios between 1 and 3, indicated the same cation effect.

The positions of Hyamine 10X and lithium in this series require comment. The nitrogen atom in the Hyamine cation has attached to it a methyl, an ethyl and a benzyl group and a long carbon chain. We suggest that the positive charge is localized around nitrogen and that the long chain is oriented away from the nickel atom. Hence this cation would appear to be a little greater in size than the tetraethylammonium cation. Since the dielectric constant of dimethyl sulphone is around 40<sup>25</sup> we expect that a solution of lithium chloride contains a high concentration of solvated lithium ions which are, effectively, larger than the other cations studied. Thus, we conclude that the above order of formation parallels that of increasing cation size.

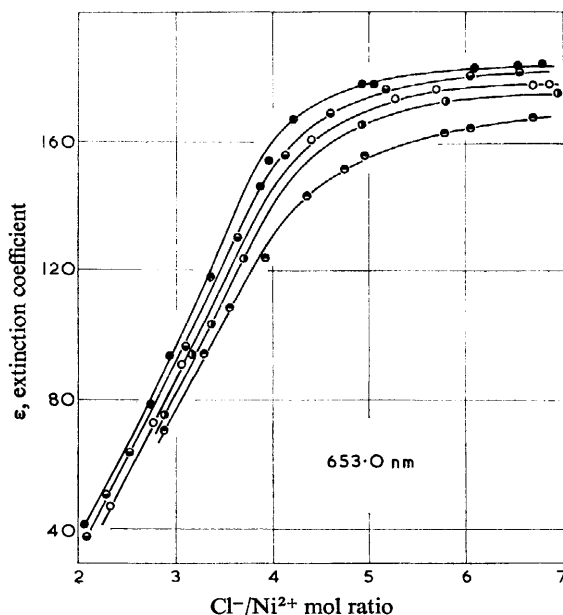


FIG. 5.—Mol ratio plot at 653.0 nm in dimethyl sulphone.

●,  $(\text{CH}_3)_4\text{N}^+$ ; ◐,  $(\text{C}_2\text{H}_5)_4\text{N}^+$ ; ○,  $(\text{C}_4\text{H}_9)_3(\text{C}_6\text{H}_5\text{CH}_2)\text{P}^+$ ; ●,  $(\text{C}_6\text{H}_5)\text{As}^+$ ; ○,  $\text{Li}^+$ .

The cation effects in dimethyl sulphone are less marked than in acetone and the higher dielectric constant of the medium suggests that instead of solvent shared ion-pairs being formed, solvent separated ion-pairs<sup>26</sup> are present in solution and could account for the observed phenomena.<sup>25</sup> All the solutions studied were too weak for polymer formation to be considered a viable concept; it has not previously been evoked to explain nickel-halide complex formation in solvents of low coordinating power.

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