# The Solvation of Iron (III) By 1-Methyl-2-Pyrrolidinone

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*Abstract*

Evidence has been obtained indicating that the strength of solvation of water and 1-methyl-2-pyrrolidinone with iron (III) is of approximately the same magnitude. Under certain conditions, one molecule of 1-methyl-2-pyrrolidinone apparently can replace one molecule of water in the solvation sphere. The equilibrium constant has been estimated using a spectrophotometric method.

Rollinson and White (5) have studied some chromium (III)-amide complex compounds, including tris-(1-methyl-2-pyrrolidinone)-trichlorochromium (III). On the basis of a shift of the carbonyl band to slightly lower frequencies in the infrared spectrum, the coordination appears to be through the oxygen atom of the amide. A steric effect was reported to exist between the coordinated 1-methyl-2-pyrrolidinone ligands (1).

Madan and Sturr (3) found that transition metal complexes with 1-methyl-2-pyrrolidinone readily hydrolyze in water. The purpose of the present study was to determine if iron (III) perchlorate in aqueous solution could accept any 1-methyl-2-pyrrolidinone molecules in its sphere of solvation. The extent of reaction would be expected to be quite small because of the ease of the reverse reaction (3). If, however, the 1-methyl-2-pyrrolidinone does replace any water molecules in the sphere of solvation, the absorption spectrum would be expected to change. Spectrophotometric absorption in different solvents has been discussed (4).

The complexes of 1-methyl-2-pyrrolidinone with transition metals have been studied quite extensively in the solid form (1, 3, 5); however, few studies have been made with aqueous solutions. The o-tolyl biguanide complexes of some transition metal ions in 1-methyl-2-pyrrolidinone have been investigated (7).

## Experimental

Solutions of iron (III) perchlorate and 1-methyl-2-pyrrolidinone were prepared in highly purified water. The water was distilled and then passed through two Illco-Way research model ion exchange columns. The iron (III) perchlorate was purchased from the G. Frederick Smith Chemical Company. The 1-methyl-2-pyrrolidinone was the Spectroquality reagent supplied by Matheson, Coleman and Bell.

A series of isomolar solutions was prepared for study by the method of continuous variations (2).

A Cary Model 14, a Beckman DU, and a Perkin-Elmer Model 202 recording UV-visible spectrophotometer were used to obtain spectra

of solutions containing iron (III) perchlorate, 1-methyl-2-pyrrolidinone, and mixtures of metal ion plus ligand. All data were obtained using 1-cm cuvettes. The temperature was approximately 25°C.

## Results and Calculations

The stability of mixed solutions was tested by scanning spectra at certain time intervals after mixing of freshly prepared solutions. Data for solutions containing 0.2M Fe(III) plus varying amounts of 1-methyl-2-pyrrolidinone (1-M-2-P) indicate that the solutions were relatively stable with the greatest drifting usually detected after 6 to 24 hours, (Table 1). Therefore, all solutions used in further studies were freshly prepared, and all spectra were scanned as soon as possible after mixing of solutions.

TABLE 1. *Absorbance data at 520 nm for Fe (III) plus 1-methyl-2-pyrrolidinone as measured at specified time intervals.*

| Time (Hours) | 0.2M Fe (III) 0.1M 1-M-2-P | 0.2M Fe (III) 0.2M 1-M-2-P | 0.2M Fe (III) 0.4M 1-M-2-P | 0.2M Fe (III) 1.0M 1-M-2-P |
|---|---|---|---|---|
| 0 | .214 | .219 | .240 | .282 |
| 1 | .218 | .221 | .239 | .287 |
| 2 | .216 | .222 | .238 | .286 |
| 6 | .210 | .222 | .231 | .269 |
| 24 | .205 | .212 | .235 | .276 |

The data for an isomolar system of iron (III) perchlorate and 1-methyl-1-pyrrolidinone (Table 2) indicate the formation of a 1:1 complex. It would appear that under certain conditions one molecule of 1-methyl-2-pyrrolidinone could replace one molecule of water; however, a series of solutions made with Fe(III) nitrate and 1-methyl-2-pyrrolidinone indicated the possible formation of a dimer of the formula, $Fe_2(1\text{-M-2-P})^{+3}$.

TABLE 2. *Absorbance data at 430 nm for isomolar solutions of iron (III) perchlorate and 1-methyl-2-pyrrolidinone.*

| Concentration Fe (III) | Concentration 1-M-2-P | Absorbance at 430 nm |
|---|---|---|
| 0.00 | 0.20 | 0.000 |
| 0.04 | 0.16 | 0.447 |
| 0.05 | 0.15 | 0.540 |
| 0.10 | 0.10 | 0.806 |
| 0.15 | 0.05 | 0.727 |
| 0.20 | 0.00 | 0.289 |

The data in Table 3 were obtained under conditions which appeared favorable for the formation of $Fe(1\text{-M-2-P})^{+3}$. Mixtures of iron (III) perchlorate and 1-methyl-2-pyrrolidinone were made at the

concentrations listed in Table 3. These data were analyzed by the method of Siefker (6) for the calculation of an equilibrium constant for the reaction:

$$Fe(H_2O)_x^{+3} + \text{1-M-2-P} = Fe(\text{1-M-2-P})\ (H_2O)_{x-1}^{+3} + H_2O$$

TABLE 3. *Absorbance data at 470, 480, 490, and 500 nm for solutions containing 0.06 M iron (III) perchlorate and varying concentrations of 1-methyl-2-pyrrolidinone.*

| Concentration 1-M-2-P | 470 nm | 480 nm | 490 nm | 500 nm |
|---|---|---|---|---|
| 0.00 | .151 | .191 | .232 | .271 |
| 0.03 | .156 | .197 | .244 | .292 |
| 0.06 | .158 | .198 | .243 | .297 |
| 0.12 | .160 | .208 | .257 | .317 |
| 0.18 | .169 | .218 | .277 | .347 |
| 0.24 | .168 | .222 | .283 | .354 |
| 0.30 | .175 | .232 | .299 | .388 |
| 0.36 | .172 | .240 | .310 | .410 |
| 0.42 | .175 | .237 | .310 | .430 |
| 0.48 | .182 | .247 | .327 | .436 |
| 0.54 | .195 | .251 | .341 | .462 |
| 0.60 | .202 | .272 | .367 | .502 |
| 0.72 | .207 | .282 | .385 | .533 |
| 0.84 | .214 | .291 | .401 | .570 |
| 0.90 | .218 | .298 | .416 | .589 |
| 1.08 | .221 | .310 | .434 | .628 |
| 1.20 | .230 | .323 | .462 | .672 |
| 1.50 | .242 | .346 | .500 | .742 |
| 1.80 | .255 | .370 | .548 | .824 |

The absorbance data were corrected for the absorption of light by the hydrated iron (III) remaining in the solution. This was done by iterations of the calculations with the computer method (6). The result of the calculations indicated that 1-methyl-2-pyrrolidinone replaces water in the sphere of solvation or iron (III) only slightly. The equilibrium constant for the reaction given above was found to be approximately unity.

## Literature Cited

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