Investigation of
Cupric Chloride in Acetonitrile

Ch 80 Project. Third Term.

1961-2

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Introduction:

The original purpose of this investigation was to compare by spectrophotometric means acetonitrile solutions of the transition metals with aqueous solutions of these metals, and to resolve any anomalies by means of ligand-field theory. However, experimental results with cuprous chloride were so confusing as to be unresolvable in a rigorous manner. For example, extinction coefficients and peak positions were found to change with time in an unobvious fashion, different peaks changing in perhaps related ways but in inconsistent fashion. Further, addition of water, chloride ion, and pyridine also had quite unexplainable effects.

As a consequence of the inexplicability of the initial results, the focus of the investigation was shifted to attempts to discover a rationale for earlier inexplicable results. Unfortunately, this aim was not successful and this investigator is unable to present more than a summary of experimental results and the observation that the changes in extinction coefficients and peak positions with time, water, chloride ion, and pyridine content are not simply related.

Preliminary Investigation:

Spectra were taken of a solution 0.0095M in $CuCl_2$[1] and a solution 0.0076M in $CuCl_2 \cdot 2H_2O$ and of solutions 1/20 the concentration of these (0.000475M and 0.000380M, respectively). For the $CuCl_2$ the following extinction coefficients were obtained:

ϵ :	3.43×10^3	5.43×10^2	7.38×10^1
λ :	3130A	4610A	8700A

For $CuCl_2 \cdot 2H_2O$:

ϵ :	4.26×10^3	6.52×10^2	9.34×10^1
λ :	3120A	4600A	8760A

These spectra were almost exactly identical in actual peak heights, but since the concentrations were different, the apparent ϵ's are not identical. Thus there is some question about the validity of the data, (i.e., the operator probably made the mistake of rerunning the same solutions).

Eight days later a spectrum of the $CuCl_2 \cdot 2H_2O$ showed a change in ϵ's.

ϵ :	2.71×10^3	1.03×10^3
λ :	3130A	4640A

These solutions were found to obey Beer's Law. (Figure 1)

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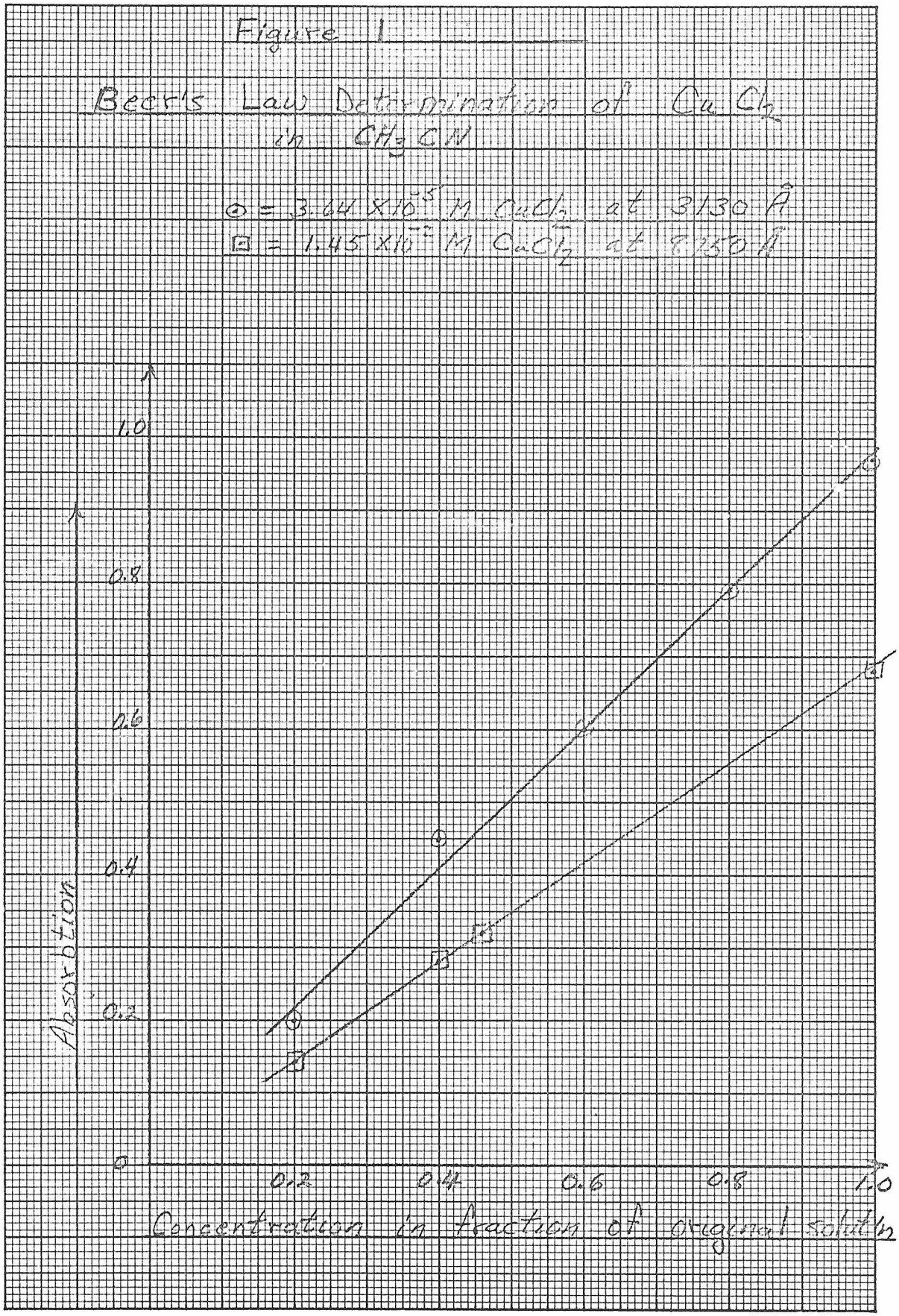
(1) All solutions are in spectral grade acetonitrile, and all spectra were taken on the Cary 14 spectrophotometer.

Figure 1

Beer's Law Determination of $CuCl_2$ in CH_3CN

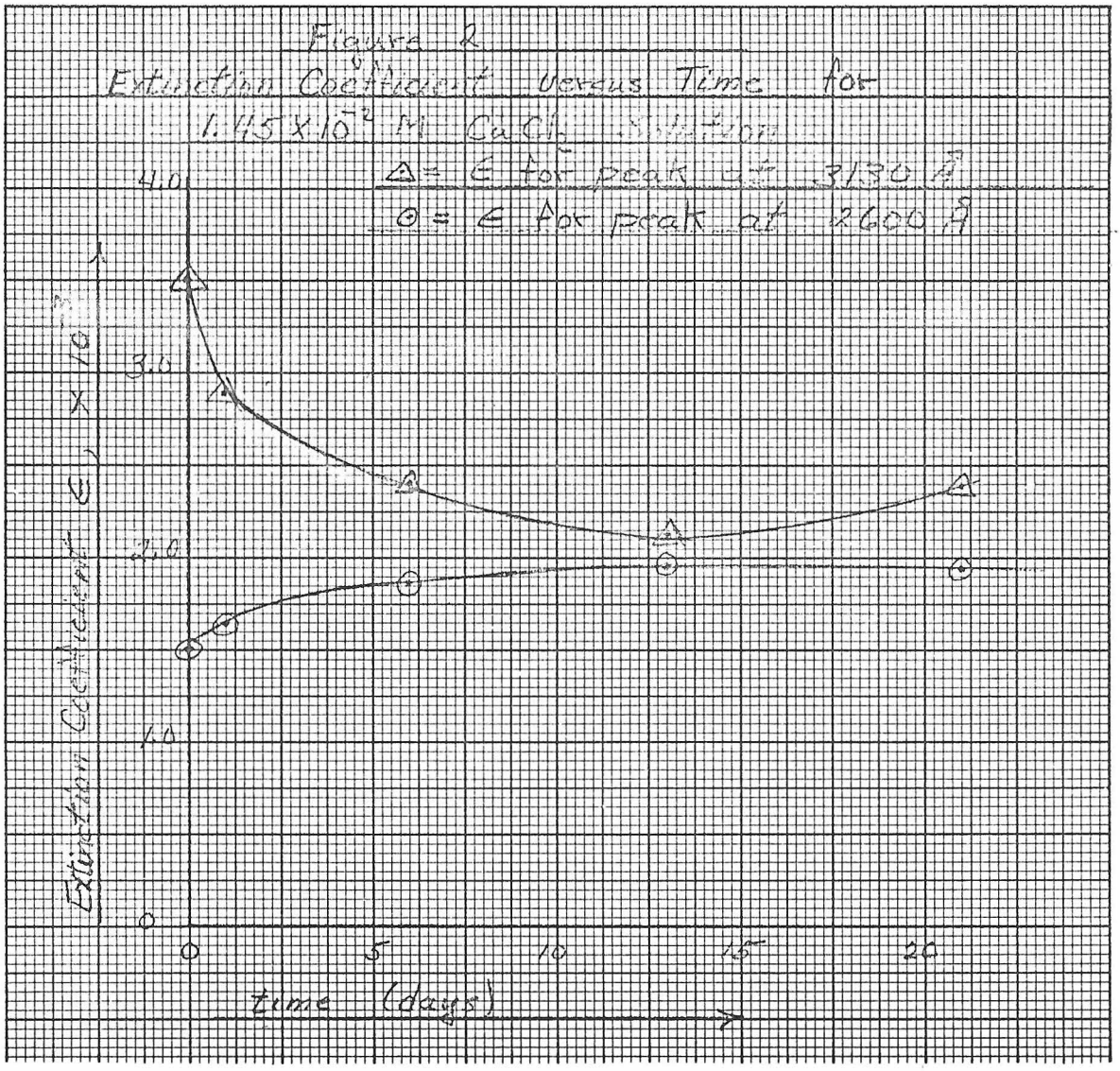
○ = 3.64×10^{-5} M $CuCl_2$ at 3130 Å

□ = 1.45×10^{-5} M $CuCl_2$ at 8250 Å



Slow change in ϵ for $CuCl_2$ with time:

A new solution of anhydrous $CuCl_2$ was made, 0.0145M.



For the peak at 4600A:

$\epsilon x10^{-2}$	5.22	8.24	8.37
t (days)	0	13	21

There was a peak originally at 8700A, ϵ of 76.2, which after twenty-two days had shifted to 8850A and dropped to an ϵ of 48.1 and split and broadened. The peak at 2600A is a shoulder

on a peak at lower λ after twenty-two days. This data indicates that this peak at lower λ rises strongly with time, and the evident behaviour of the 2600A peak is at least partly attributable to the influence of the peak at lower λ.

Effect of the addition of water:

Water was added in various amounts in order to try to see if the changes in the spectra over time were due to changes in water concentration; $CuCl_2$ is 3.64×10^{-4}M.

In figure 3 the peak at 3000A disappears at 10% H_2O by volume, and at more than 2.2% H_2O the peak at 2600A becomes merely a bump on a rising peak at lower λ.

For the peak at 4600A:

$\epsilon \times 10^2$	5.22	4.81	1.67	peak disappears
$\%H_2O$	0	2.2	4.0	6.0

For the peak at 8700A:

λ	ϵ	$\%H_2O$ by volume
8850	54.9	0
8500	42.5	10

We see that for these peaks at 4600 and 8700A the general behaviour is similar for increases in water content and for aging of the solutions, except that in the aging curves we have the tails of the curves turning back after a time.

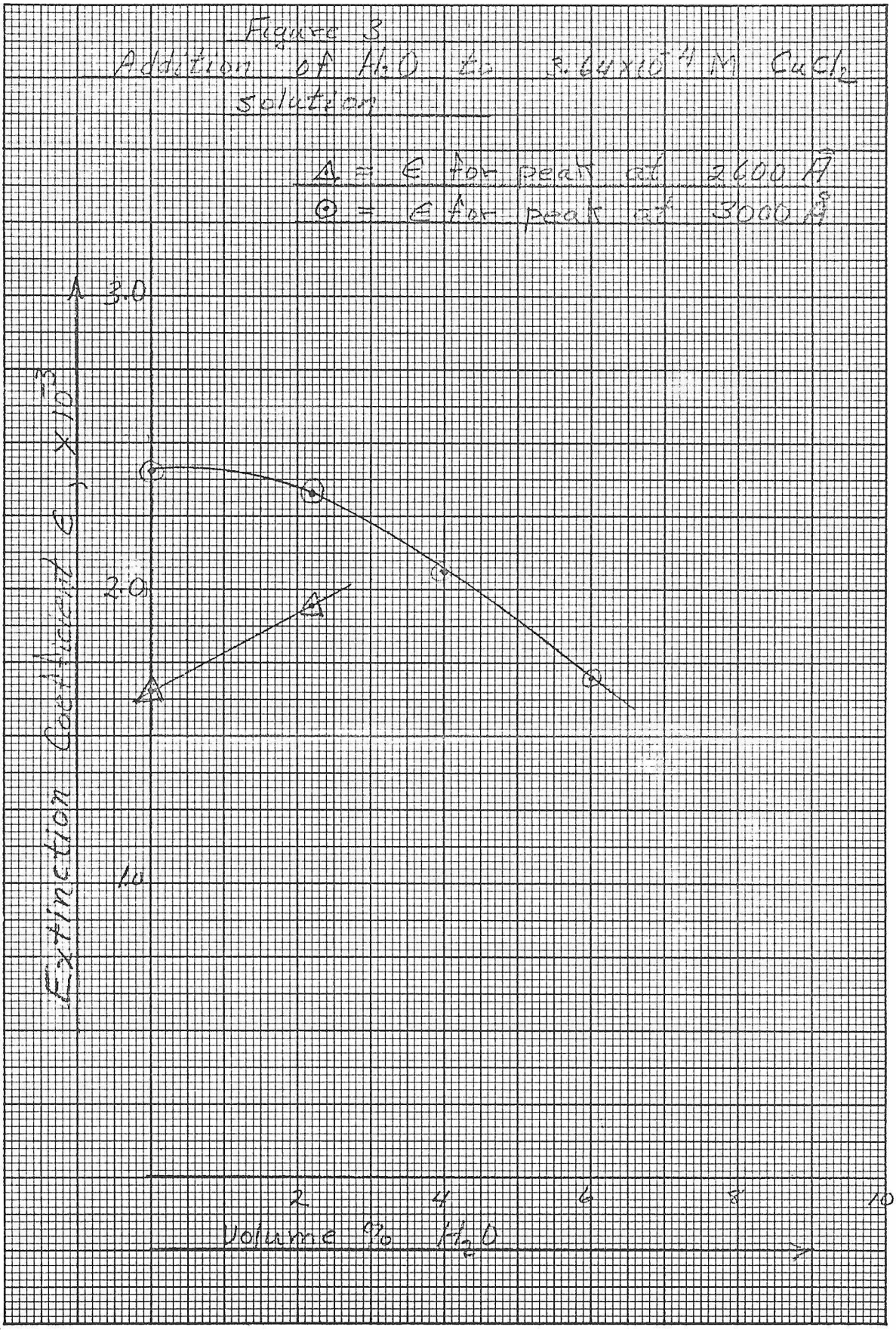
However, the peak at 4600A decreases with increasing H_2O content, while this same peak showed increased ϵ with aging. Further, we see that the peak at 8850A doesn't drop much with added H_2O, but it shifts to a lower λ instead of a higher one, as in the aging situation.

Figure 3

Addition of H_2O to 3.64×10^{-4} M $CuCl_2$ solution

△ = ε for peak at 2600 Å

⊙ = ε for peak at 3000 Å



Effect of the addition of lithium chloride:

Since the behaviour of the peaks with aging was not fully resolved by comparison with the effects of added water, the effect of added chloride ion was investigated. A solution was prepared 3.64×10^{-4}M in $CuCl_2$, and spectra were taken after the addition of various amounts of LiCl. (Figure 4.)

These results did not contribute much to the resolution of the problem, so LiCl was added to a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ in CH_3CN in order to observe the effect of less than two equivalents of chloride per equivalent of cupric ion.

The peak at 3000 was barely visible with no LiCl added and there was a low broad peak around 7750A, ϵ of 21.4. But when ~1/2 an equivalent of LiCl was added to one equivalent of $Cu(ClO_4)_2 \cdot 6H_2O$, the peak at 3000 went off scale and the peak at 7800A increased ϵ to 60.4. While interesting, this result did not shed any light on the problem of the other changes with time, $Cl^{\ominus}$ concentration, and H_2O content.

When approximately 500 equivalents of LiCl were added to one equivalent of $CuCl_2$, the far peak shifted to 8870A, $\epsilon = 57.1$, with broadening and splitting similar to that shown after twenty-two days with $CuCl_2$. Thus, at this point it would seem that the peaks at 2600 and 3130A are related as a first approximation to the H_2O content and the peak at 4600A is certainly not related to H_2O content, while the one at 8850A appears to be related to chloride complexes which reach equilibrium slowly.

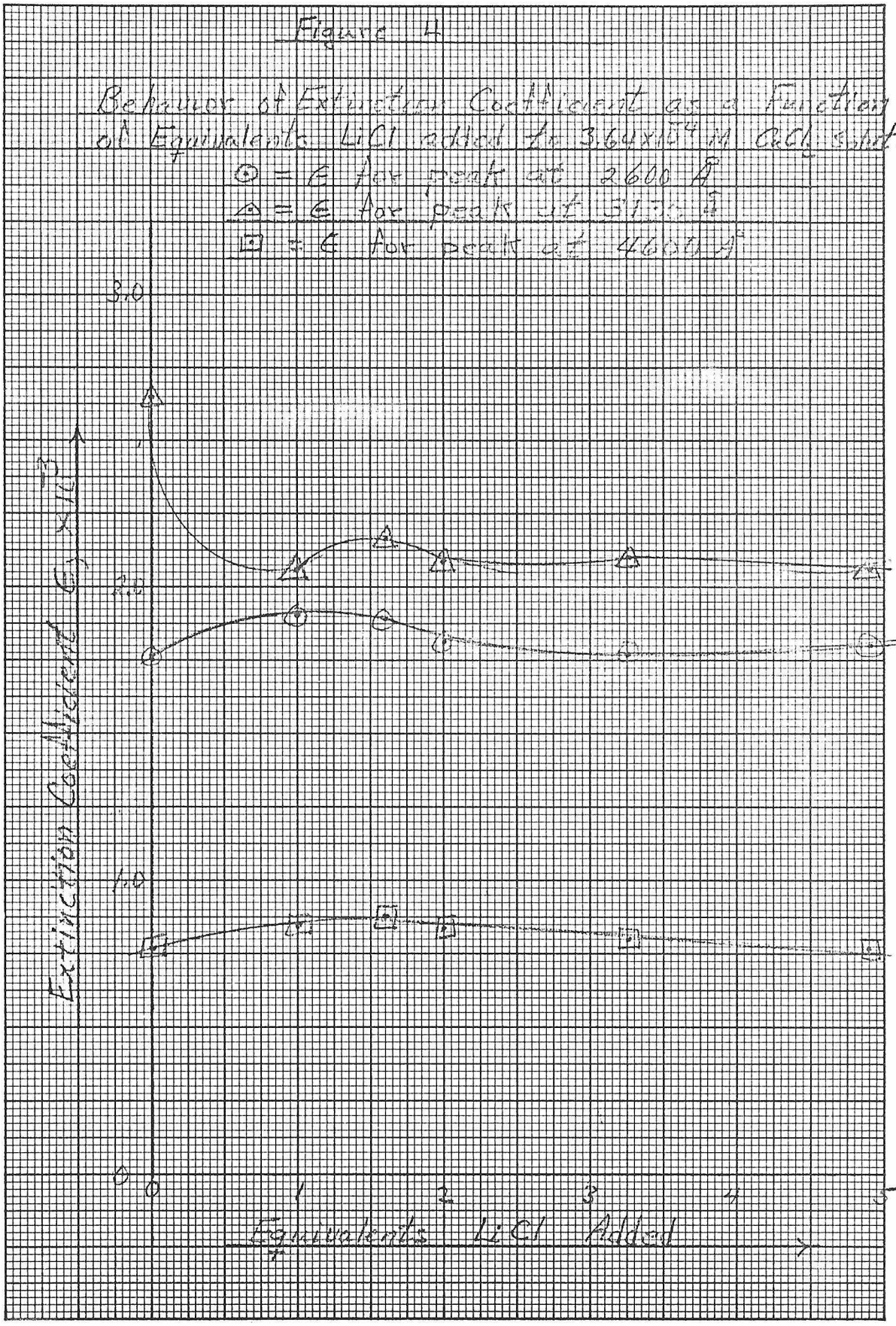
Figure 4

Behavior of Extinction Coefficient as a Function of Equivalents LiCl added to 3.64×10^{-4} M CoCl$_2$ solution

○ = 6 Å/sec peak at 2600 Å

△ = 6 Å/sec peak at 5150 Å

□ = 6 Å/sec peak at 4600 Å



Pyridine was also added to solutions of $CuCl_2$ and $LiCl+CuCl_2$:

Pyridine was added to solutions of lithium chloride with cupric chloride and to a solution of cupric chloride for the purpose of observing chloride ions in solution.

1 equivalent $CuCl_2$ + 1 equivalent pyridine gave:

ϵ	λ
4.67×10^3	2570
1.87×10^3	3070
5.22×10^2	4600

After one day these had changed to:

ϵ	λ
4.60×10^3	2570
0.908×10^3	3080
2.74×10^2	4600

1 equivalent $CuCl_2$ + 2 equivalents LiCl + 1 equivalent pyridine gave:

ϵ	λ
4.51×10^3	2570
2.16×10^3	3070
6.19×10^2	4600

After one day:

ϵ	λ
4.36×10^3	2570
1.18×10^3	3080
2.74×10^2	4620

Approximately 1 equivalent of pyridine was added to a

solution 1.46×10^{-3}M in $CuCl_2$, giving high absorption from 2000 to 3200A (off scale) and $\epsilon = 2.83 \times 10$, @ 4600A.