CORROSION INHIBITION WITH QUATERNARY AMINES

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By

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INTRODUCTION

Two reactions are involved when a steel coupon is placed in acid solution. One is iron dissolution and the other reaction is hydrogen evolution. These occur at different sites on the metal, which are referred to as "local cathode" and "local anode." Thus:

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad \text{Anodic Reaction}
\]

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad \text{Cathodic Reaction}
\]

For metal, it is at the anode that corrosion takes place, and both the anodic and cathodic reactions occur in one electrode, which is the metal surface (1). Therefore, metal surface consists of many anodic-cathodic cells which are localized and control the corrosion mechanism. This is sometimes referred to as a "mixed-potential" system.

Therefore, in order to study steel corroding in acids, it is necessary to do so in terms of these two separate electrochemical reactions. In particular, we are interested in how an external potential applied to the one piece of steel will affect the two individual reactions, and also how chemicals (inhibitors) added to the acid affect these reactions. The application of a potential from outside slows up one and speeds up the other. By using a reference electrode system, we can tell how the potential of the corroding steel is changing from its open-circuit potential value.
These changes of potential with an externally applied current are called "polarization curves," and characteristics of these curves can be related to the individual iron and hydrogen reactions.

Figure (A) shows the anodic and cathodic polarization curves; the former is to the right and the latter is to the left. At point K, there is no current applied. If an external current is applied to increase the anodic current, more iron goes to solution as iron ions, and fewer hydrogen ions are converted to hydrogen molecules (curve AB). If polarity
is reversed and cathodic current is used, more hydrogen ions will go to hydrogen molecules and less iron is dissolved in the solution as iron (curve CD). At point A, there is no iron dissolution taking place, and only hydrogen evolution occurs. This point is referred to as "Reversible Iron." At point C, there is no hydrogen evolution, and iron dissolution is taking place. This point is called "Reversible Hydrogen." Somewhere in between reversible hydrogen and reversible iron, there is a point where iron dissolution and hydrogen evolution rates are the same (line FG). Extrapolation of the lines AB and CD intersects the vertical projection from the corrosion potential Y, and at this point two reactions are occurring with the same rate. Point A is called "Open Circuit Potential" and points F and G are referred to as "Open Circuit Current" for anodic and cathodic polarization curve.

If an inhibitor is added, one of several things may occur: either the slope of D changes, or the half-reaction potential shifts, or an ohmic resistance is introduced, or some combination of these occurs. The movements of these potentials and the changes in these polarization curves are normally measured against a reference electrode whose potential is known (usually a saturated calomel electrode).

The word "cathode" refers to an electrode at which current enters to the electrolyte, and "anode" as the electrode at which current leaves the electrode and
returns to the electrolyte. As mentioned before, at the open circuit potential, the rate of oxidation of iron is equal to the rate of reduction of hydrogen ions.

\[ I \text{ (iron)} = I \text{ (hydrogen ion)} \]

If current is impressed on a cell from an external source, such as a potentiostat or battery, the steady state potential is disturbed and the above equilibrium no longer exists. The difference between the actual reversible and irreversible potential is called overvoltage. The irreversible potential of an anode is more positive than its reversible potential. When the applied potential is infinitesimally more positive than the reversible potential of the electrode, we have

\[ E_{\text{anode, irreversible}} = E_{\text{rev.}} + \eta_{\text{anodic}} \]

where \( \eta \) is anodic overpotential.

If the external potential is only infinitesimally more negative than the reversible electrode potential, it can be written as

\[ E_{\text{cathode, irreversible}} = E_{\text{rev.}} - \eta_{\text{cathode}} \]

Plots of the external current vs. the overpotential, \( \eta \), are called "polarization curves," and the effects of inhibitors on these curves can be interpreted in terms of which of the two electrochemical reactions is changed.

**Adsorption Background**

Inhibitors (usually organic nitrogen compounds) added
to the acid may become attached to the metal surface
(adsorbed) and affect one or both of the two electro-
chemical reactions.

There are two types of adsorption by metal surface: one
is Van der Waals forces of adsorption, which are physical
forces; the other one is chemical adsorption (chemisorption),
which forms chemical bonds between organic compound and
metal surface. Physical adsorption is generally accompanied
by small heat change, that is, 5 kcal or less per mole,
while in chemical adsorption heat involved is from 10 to
100 kcal per mole.

The mechanism of adsorption of inhibitors on metal
surface could be by either physical adsorption or chemi-
sorption. In nitrogen-containing compounds where there is
a free pair of electrons, the electron density on the nitro-
gen and its availability cause a bond formation between
metal surface and organic molecules by sharing an electron
pair from the inhibitor \( \text{R-N} \). This is referred to as "chemi-
cal adsorption," where metal acts as an acceptor, and inhi-
bitor as a donor. In quaternary ammonium compounds, there
is no free electron pair present, and organic inhibitor ex-
ists in acid solution as cation \( \text{R-N}=\text{H}^{+} \) and nitrogen has
formal positive charge as \( \text{R-N-H}^{+} \), where \( \text{R} \) could be any
aryl or alkyl group. In such a case where nitrogen is pos-
itive, it must be adsorbed physically on the metal surface,
and forms a film, by virtue of electrostatic attraction.
This adsorption should occur at the local cathode, since
attracted there. There is a direct relationship between this film resistance and inhibition efficiency (5,6). If, however, the inhibitors exist as free amines in solution, they should adsorb at the local anode (7). In most inhibitors in acid solutions, there is an equilibrium

$$\text{RNH}_2 + \text{H}^+ \rightleftharpoons \text{RNH}_3^+$$

so that either the free base form (RNH$_2$) or the cation form (RNH$_3^+$) could adsorb, and the equilibrium would be displaced to replenish the supply. However, for quaternary compounds $$\text{RNH}_4^+ \text{Cl}^-$$

there can be no equilibrium, and the adsorption ought to be just physical, and only the local anodes should be affected. The purpose of the present work was to study the electrochemical and inhibition effects of several quaternary compounds in the acid corrosion of steel.

Quaternary ammonium compounds are salts and are very soluble in most of the solvents. That is why a wide range of concentration of them can be used without any difficulty. The recent studies of these compounds have reported that N-alkyltrimethyl-ammonium bromide inhibits the acid dissolution of the steel (8). The degree of inhibition increased with alkyl chain length between 4 and 18 carbon atoms. No polarization curves were given in this study.

Experimental Procedures

The mild steel coupons which were used throughout the experiments had approximate size of 25mm x 60 mm, with one
millimeter thickness. Coupons were allowed to suspend in acid solution by a rod and about 20 inches in total area of the coupon was exposed to the solution. The acid used was 2.0 M HCl at 60 degrees centigrade. The coupon surfaces were polished with fine emery paper, rinsed in acetone and distilled water. Figure (A) shows the experimental apparatus which was used.

Potentiostat

![Diagram of Potentiostat](image)

Figure (A)

Two different procedures were used to determine the rate of corrosion. In the first method the hydrogen gas evolved was collected in a gas burette and the volume was measured at given time intervals. Periodic rate determination was plotted for cathodic-anodic polarization in electrochemical process. From this method, the amount of iron converted to iron chloride could be determined. This method of rate determination was best, and it was used especially in cathodic polarization and also where the corrosion rate was high, as in the case where no inhibitor was present.
The second method was the direct weighing of the metal coupons on an analytical balance. The coupon was removed from acid, rinsed with acetone, and weighed. Test bottles used contained about 200 ml of acid solution (2M HCl), which were placed in a constant-temperature oil bath maintained at 60 degrees centigrade. Working electrode and calomel reference electrode were arranged to be close to each other in the first bottle. The second bottle was connected to the first one by salt bridge for electrolytic contact. Platinum electrode was placed as counter electrode in the second bottle for completing the electrochemical circuit. An outlet for hydrogen gas evolution was arranged to set periodic burette readings. Uninhibited polarization curves were run and the result was compared with inhibited polarization curves for corrosion rate calculations.

The inhibitors used were pyridine quaternaries of several different chlorinated hydrocarbons. The preparation and purification of these compounds are described in the appendix.

Results and Discussions

Experiments showed that the average loss of metal in an uninhibited solution was $5.13 \pm 0.76 \text{ mg l cm}^{-2} \text{ h}^{-1}$ hr., while in inhibited acid solution it was considerably less than this obtained value, depending on the type of inhibitor used. A number of different quaternary ammonium compounds were used as inhibitors. It turned out that hexadecyl pyridinium
chloride was the best one in the group, with the percentage of inhibition up to 99% in 100 ppm acid solution. The list of the used compounds are as follows (The Cl\(^{-}\) anion is not shown.):

<table>
<thead>
<tr>
<th>Structure</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\phi\text{-N}^+\text{-CH}_2\text{-}\phi)</td>
<td>Benzyl Pyridinium Chloride</td>
</tr>
<tr>
<td>(\phi\text{-N}^+\text{-CH}_2\text{-}\phi\text{-CH}_3)</td>
<td>P-Methyl Benzyl Pyridinium Chloride</td>
</tr>
<tr>
<td>(\phi\text{-N}^+\text{-CH}_2\text{-}\phi\text{-C}_4\text{H}_9)</td>
<td>P-Butyl Benzyl Pyridinium Chloride</td>
</tr>
<tr>
<td>(\phi\text{-N}^+\text{-CH}_2\text{-}\phi\text{-C}<em>8\text{H}</em>{17})</td>
<td>P-Octyl Benzyl Pyridinium Chloride</td>
</tr>
<tr>
<td>(\phi\text{-N}^+\text{-CH}_2\text{CH}_2\text{-}\phi)</td>
<td>Phenyl Ethyl Pyridinium Chloride</td>
</tr>
<tr>
<td>(\phi\text{-N}^+\text{-(CH}<em>2\text{)}</em>{15}\text{CH}_3)</td>
<td>Hexadecyl Pyridinium Chloride</td>
</tr>
</tbody>
</table>

The first two inhibitors were very poor inhibitors. In most cases it was impossible to determine the inhibited corrosion rate since it was so close to the uninhibited corrosion rate. Phenyl ethyl pyridinium chloride was a better inhibitor than either of the above mentioned compounds, but still it was not considered as a good inhibitor. It has the same molecular weight as P-methyl benzyl pyridinium chloride, but is much more efficient. However, the additional length of aliphatic carbon chain next to nitrogen may make a difference in the efficiency.

Within the other three organic compounds, hexadecyl pyridinium chloride was an excellent compound and even effective in concentration as low as 0.10 ppm. Table 1 shows its
effectiveness in low concentration and also in comparison to other inhibitors.

TABLE 1

INDIRECT ACTION OF SOME QUATERNARY AMMONIUM

<table>
<thead>
<tr>
<th>Concentration PPM</th>
<th>Compound</th>
<th>1000</th>
<th>100</th>
<th>10</th>
<th>1</th>
<th>1</th>
<th>0.01</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl Pyridinium Chloride</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>nil</td>
</tr>
<tr>
<td>2-Benzyl Pyridine</td>
<td></td>
<td>0.76</td>
<td>0.17</td>
<td>Slight</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>Hexadecyl Pyridinium Chloride</td>
<td></td>
<td>0.92</td>
<td>0.87</td>
<td>0.75</td>
<td>0.20</td>
<td>nil</td>
<td>nil</td>
</tr>
</tbody>
</table>

Typical weight loss-time curves for two of these compounds in 2.0% HCl at 60 °C are shown in Figures 1 and 2. These data illustrate a point which often causes considerable uncertainty in interpretation, namely the invariant (Figure 1) versus the continuously varying (Figure 2) corrosion rate. For well inhibited solutions, it is not at all uncommon to obtain invariant rates, while for uninhibited and poorly inhibited solutions, it is usually impossible to fix a single value of the rate for a reference value. In this
particular work, a more or less steady rate obtained after several hours of corrosion in calculating per cent inhibition values, although it is doubtful that the real surface area after this much attack is comparable to the real surface area being corroded in the well-inhibited solutions.

Ford and Riggs (?) have shown that some improvement in reproducibility of per cent inhibition values can be obtained by allowing the coupon to corrode freely in the uninhibited solution for several minutes before the inhibitor is added, and then relating rates obtained immediately before and immediately after the addition. While this increased reproducibility is desirable, it requires considerably more experimental effort, and would not add significantly to the present study, which is looking primarily for relative effects between compound types.

Inhibition data for two of the compounds tested are shown in Figures 3 and 4 as a function of concentration. Similar data were obtained for the other compounds; the data shown were chosen to illustrate the wide variation in inhibition levels while retaining the same general functional dependence on concentration. \( i \) is the fraction inhibition, \( 1 - \frac{\text{Inhibited Rate}}{\text{Uninhibited Rate}} \) analog of the fraction of surface covered by adsorbed molecules in the Langmuir adsorption isotherm. Hoar and Holliday(8) first treated corrosion data in terms of this isotherm, and found that for some inhibitors a plot of log \( \frac{\theta}{1-\theta} \) versus log (inhibitor concentration) gave a straight line of slope
FIGURE 1

LINEAR WEIGHT LOSS BEHAVIOR
STEEL IN 2.0N HCl
100ppm n-C_{16}H_{33}N^+C_{5}H_{5}Cl^-
FIGURE 2
NON-LINEAR WEIGHT LOSS BEHAVIOR
STEEL IN 2.0N HCl, 60°C
100 ppm p-C₄H₉C₆H₄-CH₂N⁺C₅H₅Cl⁻
FIGURE 4

INHIBITION-CONCENTRATION FUNCTIONS

p-C$_4$H$_9$-C$_6$H$_4$-CH$_2$-N'TC$_5$H$_5$Cl$^-$ IN 2.0 N HCl, 60°C
1.0, in agreement with the Langmuir theory. The data on the quaternaries do not follow this treatment, but instead show linear behavior when \( \frac{\theta}{1-\theta} \) itself is plotted versus log (concentration). No interpretation of this behavior in terms of isotherms can be offered at the present time.

Table 1 gives the maximum values of \( \theta \), and the corresponding values of \( \frac{\theta}{1-\theta} \), which could be obtained for each inhibitor tested. It is interesting to note how the use of the fraction \( \frac{\theta}{1-\theta} \) helps to "spread out" the effects of structure in the better inhibitors. Thus, \( \frac{\theta}{1-\theta} \) goes from \( \frac{1}{2} \) to 124, or doubles, as \( C \) itself goes from 0.935 to 0.992.

In view of the linearity of the \( \frac{\theta}{1-\theta} \) dependence on log \( C \), and also because of the importance of the fraction, in adsorption theory, it is felt that a more meaningful interpretation of the data can be made when they are analyzed in terms of this function, rather than in terms of per cent inhibition alone.

**TABLE 2**

**SUMMARY OF MOLECULAR STRUCTURE EFFECTS OF QUATERNARIES ON INHIBITION**

<table>
<thead>
<tr>
<th>Quaternary</th>
<th>( \theta_{\text{max}} )</th>
<th>( \frac{(2/1-\theta)}{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{5}H_{11}N+-(CH_{2})<em>{2}-C</em>{6}H_{4}CH_{3} )</td>
<td>0.75</td>
<td>3</td>
</tr>
<tr>
<td>( C_{5}H_{11}N+-(CH_{2})<em>{2}-C</em>{6}H_{4}C_{6}H_{9} )</td>
<td>0.91</td>
<td>10</td>
</tr>
<tr>
<td>( C_{5}H_{11}N+-(CH_{2})<em>{2}O</em>{6}H_{4}-C_{6}H_{17} )</td>
<td>0.932</td>
<td>124</td>
</tr>
<tr>
<td>( C_{5}H_{11}N+-(CH_{2})<em>{2}O</em>{6}H_{5} )</td>
<td>0.985</td>
<td>61</td>
</tr>
<tr>
<td>( C_{5}H_{11}N+-(CH_{2})<em>{15}-CH</em>{3} )</td>
<td>0.993</td>
<td>125</td>
</tr>
</tbody>
</table>
It was expected at the beginning of this work that only
the hydrocarbon character of the inhibiting molecule would be
a determining factor in inhibition efficiency, and that hydro-
carbon character would be simply dependent on the number of
carbon atoms in the chain attached to the pyridine nitrogen
atom. The basis for this expectation was that since these
molecules did not have free electron pairs, the adsorption
process would be purely physical (2), and the many subtle fac-
tors of molecular structure which influence the chemisorption
bond would be of no effect. While the structural factors ex-
amined in the present series of compounds are limited, the ta-
ble shows that location of the phenyl group relative to the
quaternary nitrogen is a significant factor in the inhibition.
Thus, for the same hydrocarbon number, $C_6H_5-CH_2\text{CH}_2\cdot$, the ar-
rangeent with one $\text{CH}_2$ between the pyridine nitrogen and the
phenyl group yields a much poorer inhibitor than the arrange-
ment with both ethylene groups between the two aromatic
groups. Investigations of other structural effects in quater-
nary types are continuing.

Electrochemical measurements, primarily the shift in cor-
rosion potential and the changes in slopes of the log (current
density), potential curves (tafel slopes) can be interpreted
in terms of the relative effects of the inhibitor on the ano-
dic or cathodic sites of the corroding surface. Again, based
on adsorption theory, one would expect that the quaternaries,
with their formal positive charge, would adsorb preferentially
on cathodic sites and give a potential shift toward the reversible Fe/Fe' half-cell (i.e., an "anodic shift"). This was not observed by Jenkins (4) with the quaternary bromides in H$_2$SO$_4$, nor by us with quaternary chlorides in HCl. Figure 5 shows the magnitude of the shift in corrosion potential as a function of concentration of n-hexadecyl pyridinium chloride, and that it is in the direction of the reversible hydrogen electrode, thus a "cathodic shift." Jenkins' values for the quaternary bromides in H$_2$SO$_4$ gave a very similar concentration behavior, but a generally higher total potential shift (60-70 mV at $10^{-2}$ vs Sce 30). Whether the different magnitude may be an effect of the bromide ion vs. the chloride ion, or of a counter ion in the inhibitor different from the acid anion, which would seem to be constrained to adsorb, physically, early give the cathodic shift which has long been a primary argument for chemisorption.

A second electrochemical measurement often used to characterize inhibitor action is the change in Tafel slope upon addition of the inhibitor. Results for 20-ppm n-hexadecyl pyridinium chloride are shown in Figures 6 and 7 for cathodic polarizations, and in Figures 8 and 9 for anodic polarizations. These curves were obtained by measuring both the net external current (the usual polarization curve) and the partial (or half-cell) current by chemical analysis. Measurement by chemical analysis provides the polarization curve for each half-reaction well down into the corrosion potential region, in fact, past the open circuit corrosion
ELECTRODE POTENTIAL, VOLTS vs. S.C.E.

Log Molarity of n-Hexadecylpyridinium Chloride

Inhibitor Addition
Potential with Shift of Corrosion

Figure 5
FIGURE 6
CATHODIC POLARIZATION
STEEL IN 2.0N HCl

- FROM NET CURRENT
- CHEMICALLY FROM $H_2$

POTENTIAL, VOLTS vs. S.C.E.

$E_{corr.}$
FIGURE 7
ANODIC POLARIZATION
STEEL IN 2.0N HCl
FROM NET CURRENT
CHEMICALLY FROM Fe

POTENTIAL, VOLTS vs. S.C.E.
FIGURE 8
CATHODIC POLARIZATION
STEEL IN 2.0M HCl +
20ppm n-C_{16}H_{33}N^+C_5H_5Cl^-
Figure 9
Anodic Polarization
Steel in 2.0N HCl + 20ppm n-C_{16}H_{33}N^+C_5H_5Cl^-
potential. This is possible because the two half-cell reactions which make up the total corrosion reaction are already polarized well into the Tafel regions at the corrosion potential.

Both the anodic and cathodic Tafel slopes for the normal polarization curves and for the chemically determined polarization curves are given in Table 3. Note that the cathodic values obtained by direct polarization are significantly higher than the 113 millivolts expected for the hydrogen evolution reaction, while the values obtained by chemical analysis are not only closer to the expected, but are much more reproducible. The values obtained by direct polarization are probably influenced significantly by concentration polarization in these regions of high impressed cathodic currents. The anodic values obtained by both chemical and electrochemical polarization methods agree with each other very well in both the inhibited and in the uninhibited systems. Since the anodic reaction is the dissolving of the iron itself, so that there can be no concentrations changes, it is not so likely that concentration polarization would be evident even at high currents.
In regard to inhibitor behavior, there is quite clearly a strong effect on the anodic reaction (Tafel slope 131 mv uninhibited to 199 mv inhibited), and apparently none on the cathodic reaction, confirming the "cathodic shift" in corrosion potentials. At present, polarization behavior studies by chemical analysis are being extended into regions very near the reversible potentials of the respective half-cell hydrogen and iron reactions. It is hoped that a careful analysis of data in these regions will yield a number for the anodic/cathodic area ratios for uninhibited and inhibited systems, since these numbers would be an even more direct measure of the anodic vs. the cathodic character of the inhibitor adsorption.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Tafel Slopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Inhibitor, Direct Polarization</td>
<td>0.132</td>
</tr>
<tr>
<td>No inhibitor, Chemically Determined Partial Currents</td>
<td>0.131</td>
</tr>
<tr>
<td>20 ppm Inhibitor, Direct Polarization</td>
<td>0.208</td>
</tr>
<tr>
<td>20 ppm Inhibitor, Chemically Determined Partial Currents</td>
<td>0.199</td>
</tr>
</tbody>
</table>

*Inhibitor is n-hexadecyl pyridinium chloride*
CONCLUSIONS

Quaternary ammonium compounds are excellent inhibitors of acid corrosion, and seem to influence the anodic partial reaction more than the cathodic. This behavior is not readily interpretable in terms of physical vs. chemical adsorption, since these compounds do not possess the free electron pair normally thought to provide the bonding for chemisorption. Increasing the hydrocarbon bulk in the inhibitor molecule markedly increases the inhibition efficiency, which is to be expected. However, modest changes in molecular structure between molecules of essentially identical hydrocarbon content also result in marked changes in inhibition efficiency, and this behavior is not consistent with the purely physical adsorption one would expect from these formally charged species. Electrochemical measurements also indicate a pronounced effect of the inhibitor on the anodic half-reaction, but very little if any on the cathodic half-reaction. In short, all the evidence obtained to date with these compounds indicate either that they are chemisorbing (but how?), or that the generally accepted evidences of chemisorption and the chemisorption theory of corrosion inhibition need some modification.
LIST OF REFERENCES

APPENDIX I

Synthesis of the Quaternary Inhibitors

The Synthesis of Benzyl Pyridinium Chloride

This synthesis, the only one found in the literature, required taking benzyl chloride and pyridine in equal amounts and refluxing in an alcoholic media for ten hours at 90 °C. The liquid is evaporated, leaving benzyl pyridinium chloride.

A preliminary experiment was tried to see what the rate of formation of benzyl pyridinium chloride (PPCl) was. After the pyridine was distilled, it was mixed with benzyl chloride and after about one hour crystals formed. Recrystallization was tried with various solvents. It was insoluble in hexane, ether, and acetone, and extremely soluble in water and all alcohols.

The first try to make a large amount of the compound involved using hexane as a solvent. Thirty-eight and nine-tenths grams pyridine were mixed with sixty-two grams of benzyl chloride which was added drop-wise and refluxed for about one hour. The odor of pyridine still prevailed. Recrystallization of the material from isopropyl alcohol proved unsuccessful.

A second try using isopropyl alcohol as a solvent and refluxing at 130 °C for 7.5 hours produced a brownish viscous material. After sitting for two weeks, crystals formed and were filtered. Recrystallization from ethanol produced oily
drops in which crystals did not come out of solution. Another try using acetonitrile as a solvent produced crystals more rapidly.

After close observation it was noticed that the BPCL was very deliquescent. Thus ether was used to dissolve the impurities and keep the BPCL as a solid. After the impurities were removed, the compound was quickly placed in a desiccator with sulfuric acid as a desiccant. A typical yield was seventy per cent.

A silver nitrate titration by Fajan's method for chloride determination showed 17.3% chloride which is also the calculated percentage.

Synthesis of N-Hexadecyl Pyridinium Chloride

Twenty grams of pyridine and sixty grams of N-Hexadecyl Chloride were refluxed for seven hours at 145 C in no solvent. A brownish semi-solid with a pyridine residue remained. This was recrystallized from water and isopropyl alcohol to no avail. The remaining crystals were rinsed in ether and the dried non-deliquescent crystals were placed in a desiccator.

Fajan's method failed on this compound whose yield was 50% because the crystals turned the water brown and the endpoint could not be seen. But an infrared analysis showed up exactly as the standard N-Hexadecyl Pyridinium Chloride from Eastman #P5361.
Synthesis of 2-Ethylbenzene Pyridinium Chloride

Twenty grams of pyridine and 35 grams of 2-chloroethylbenzene were mixed in acetonitrile and refluxed at 130 °C for ten hours. White crystals formed, were filtered, and were dried. The melting point was found to be 103 °C and the chloride percentage was 17.1% where the calculated is 16.2%. Yield was 20 grams.

Synthesis of 3-Propylbenzene Pyridinium Chloride

Twenty grams of pyridine and 43 grams of 3-chloro-propylbenzene were mixed in acetonitrile and refluxed for ten hours at 120 °C. After three weeks without crystallization, seeding was tried with benzyl-pyridinium chloride and 2-ethyl-benzene pyridinium chloride to no avail. The acetonitrile was evaporated and two phases appeared. The denser phase (brownish with a pyridine smell) amounted to 9ml while the lighter yellow phase had about 60ml. Both phases were sent to an IR analysis.