Kinetic Study of the Oxidation of $\varepsilon$-Caprolactam Impurities with Permanganate for PZ Estimation

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Abstract: The permanganate number, PZ, is usually used to characterize the behavior of $\varepsilon$-caprolactam during its polymerization. Impurities in $\varepsilon$-caprolactam that are quickly oxidized by permanganate decrease the PZ value and the associated $\varepsilon$-caprolactam quality. To estimate the value of PZ of an $\varepsilon$-caprolactam containing a mixture of different impurities, a knowledge of the kinetics of the reactions involved is necessary. In this study, we obtained the rate laws of the oxidation of some typical $\varepsilon$-caprolactam impurities with permanganate. We added separately to a commercial $\varepsilon$-caprolactam different amounts, ranging from 1 to 3000 ppm, of both commercial (cyclohexylamine, hexylamine, aniline, o-toluidine, p-toluidine, $\varepsilon$-caprolactone, phenol, nitrobenzene, 2-heptylamine, cyclohexanol, cyclohexene, hexylamide, and cyclohexanone oxime) and synthesized impurities (octahydrophenazine, methyl-$\delta$-valerolactam, cyclohexenone oxime, azocyclohepten-2-one, and cyclohexanone oxime). A parallel reaction network is proposed to describe the reactions between the impurities and permanganate and the kinetic parameters have been calculated by fitting the values of PZ obtained experimentally. The PZ value measured for a mixture of impurities was compared to that predicted by using the kinetic parameters, we obtained; a good agreement exists.

Keywords: permanganate number, oxidation, $\varepsilon$-caprolactam, kinetics, impurities

Introduction

$\varepsilon$-Caprolactam is an important intermediate primarily used in the production of nylon 6 fibers and resins. Production of $\varepsilon$-caprolactam usually starts with cyclohexane oxidation to form cyclohexanone [1]. The latter compound reacts with hydroxylamine, producing the oxime, which yields $\varepsilon$-caprolactam after a Beckmann rearrangement step in oleum media [2,3]. A significant amount of effort has been exerted recently to replace cyclohexane with phenol or cyclohexene and to decrease or avoid the formation of ammonium sulfate as by-product [4].

Most of the uses of $\varepsilon$-caprolactam depend on the type and amount of impurities that it contains [5]. Consequently, it is necessary to pay attention to the purification process to ensure low enough values of these impurities. Because of the great number of chemical transformations and separation steps that are required to transform the raw materials into $\varepsilon$-caprolactam, the impurities can be formed at any stage of the process. Moreover, the purification of either the intermediates or end products constitutes a major part of the equipment required in $\varepsilon$-caprolactam plants, in addition, the purification methods depend on the impurities that are necessary to be removed.

Important differences in the type and concentration have been observed for the impurities obtained during $\varepsilon$-caprolactam manufacture [6-12]. The characterization of the quality of the $\varepsilon$-caprolactam by means of the quantification of its impurities is a complex task even though great advances have been achieved in the analytical techniques. Thus, some global parameters have been standardized and used in the literature to characterize $\varepsilon$-caprolactam purity in relation to its behavior during polymerization. Standard procedures, such as the determination of the permanganate number (PZ) [13], the volatile bases content (VB) [14], and the color or absorption at a given wavelength (UV) [15], have been employed to characterize the quality of the $\varepsilon$-caprolactam.

The PZ number is defined as the time required for a standard $\varepsilon$-caprolactam-permanganate solution to reach

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the color of a permanganate reference solution. Consequently, this parameter decreases if the rate of the oxidation of the impurities increases. If the ε-caprolactam contains impurities possessing functional groups that can be oxidized quickly by permanganate, the PZ number will be small and a poor behaviour for the ε-caprolactam during polymerization can be presumed [16,17]. The minor impurities can be quite difficult to identify and the major impurities can overlap with them. However, if a minor impurity is quickly oxidized it could have the largest effect on the decrease of the permanganate number. Because of this phenomenon, the permanganate number, PZ, is chosen as the most useful parameter to represent the quality of the ε-caprolactam and can indicate level of ε-caprolactam purification that has been achieved [7,18,19].

The color change in the standard permanganate-ε-caprolactam solution can be related to the appearance of a reduced manganese species obtained from permanganate. Therefore, the PZ number will correspond to the time required to obtain a certain conversion of permanganate in the standard permanganate-ε-caprolactam solution, which yields a specified concentration of these manganese species. The mechanism of the permanganate oxidation of organic compounds was reviewed extensively by Fattiadi (20). Potassium permanganate is one of the most versatile and vigorous among the usual oxidants and it is employed extensively in neutral media. The oxidation with permanganate occurs through several different reaction pathways: electron exchange, hydrogen atom abstraction, and direct donation of oxygen [21]. Between pH 3.5 and 12, permanganate generally undergoes a three-electron exchange and manganese dioxide is the product in the reduction.

The extent and the facility of the oxidation by permanganate ions depend on the nature of the organic compound. Aqueous potassium permanganate is a classical and selective oxidizing agent for unsaturated compounds; thus, aromatic and other unsaturated compounds are easily oxidized (particularly if the impurity is functionalized with donor groups). In contrast, saturated compounds and aromatic compounds functionalized with electron-attracting groups are hardly oxidized by permanganate. A number of papers describe the kinetics of the oxidation of several organic compounds by permanganate [22-30].

To estimate the PZ value of an ε-caprolactam sample, the rate laws of the produced transformations are needed. These rate laws depend on the specific constant, the permanganate and impurity concentrations, and their respective reaction orders. The kinetic knowledge of the reaction between the impurity and the permanganate, by means of this rate law, is a helpful tool to establish the purification grade needed.

To reach the PZ value when there is only one impurity reacting with permanganate, the initial impurity concentration must be high enough to produce the required concentration of the reduced manganese species corresponding to this PZ value and, at this time, the impurity has been partially converted. A low value of the PZ number obtained by adding an impurity may be due to either a high rate constant or a high impurity concentration.

For a complex system containing many impurities competing for the permanganate the kinetic model of the reaction network must be determined to predict the PZ value. To create this model, a rate law for each parallel reaction from the scheme can be obtained by the addition of each impurity separately.

Changes in both the raw material and the main steps (oximation or Beckmann rearrangement) to produce ε-caprolactam make it necessary to look into the new impurities produced and their effect on ε-caprolactam. Qualitative information about the influence of typical ε-caprolactam impurities on the PZ value has been published recently [16]. Usually, the information about the influence of the impurities on the permanganate number has been limited to correlations between the amount of impurities and the permanganate number for a narrow range of concentrations [7,17]; data obtained from commercial plants are not available in the literature.

In this work, the permanganate number of an ε-caprolactam containing some quantified impurities was predicted by using the individual rate laws determined for the reaction of each impurity with permanganate. Firstly, the influence of each impurity on the PZ number was quantified by adding the impurity separately, in the desired concentration, to the ε-caprolactam. This procedure provides information regarding the impurities that have the greatest influence on the permanganate number and, therefore, it points out the impurities that must be carefully controlled during the purification process. This information is also important to define the purification level needed for commercial ε-caprolactam.

**Theory: Kinetic Model of the Reaction Network**

The following parallel scheme is proposed to describe the reaction of permanganate with N oxidizable impurities of an ε-caprolactam:

\[
\begin{align*}
\text{a}_1C + M &\rightarrow b_1R_1 + k_{21}B + b_2R_2 \quad r_c &= k_cC^{b_1}M^{b_2}
\end{align*}
\]

\[
\begin{align*}
\text{a}_1I_3 + M &\rightarrow b_3R_3 + k_{23}B + b_4R_4 \quad r_{I3} &= k_{I3}I_3^{b_3}M^{b_4}
\end{align*}
\]

\[
\begin{align*}
\text{a}_2I_j + M &\rightarrow b_jR_j + k_{2j}B + b_R R_j &= k_{Ij}I_j^{b_j}M^{b_R}
\end{align*}
\]

\[
\begin{align*}
\text{a}_N I_N + M &\rightarrow b_N R_N \quad r_N &= k_{IN}I_N^{b_N}M^{b_R}
\end{align*}
\]

where the compound C is ε-caprolactam, which can contain some non-identified impurities, Ij is an added
impurity, $M$ is permanganate, $B$ is the reduced manganese species that produces the color change, and $R_j$ is an oxidized impurity. Because the complexity of the oxidation mechanism involves some manganese species, each reaction of the scheme in equation [1] lumps several elemental reactions together and, therefore, the reaction orders in the rate law can be different that the corresponding stoichiometric coefficients.

The production rate of $B$ in a batch set-up can be calculated from the scheme above as follows:

$$\frac{dC_B}{dt} = r_c + \sum_{j=1}^{n} r_j$$

(2)

The $PZ$ value is the time required to reach a fixed concentration of $B$ and $C_{B0}$. The $B$ production rate is equal to the permanganate disappearance rate. Thus, the value of $PZ$ corresponds to a fixed conversion of permanganate, $X_{M}$, if the initial permanganate concentration is constant. The $PZ$ value can be determined from equation [2] as follows:

$$PZ = \int_0^{C_{Bf}} \frac{dC_B}{k_cC_cC_{M}^{2} + \sum_{j=1}^{n} k_jC_{M}^{2j}}$$

(3)

If the conversions of permanganate and the impurity obtained at the $PZ$ time are low enough, the concentration of both species are considered as the initial values during this period. In this case, the $PZ$ value can be easily estimated for a mixture of impurities by means of equation [3] if the kinetic parameters (rate constants and reaction orders) are known:

$$PZ = \frac{C_{Bf}}{k_cC_{c}C_{M}^{2} + \sum_{j=1}^{n} k_jC_{M}^{2j}}$$

(4)

$PZ_0$ is the value obtained when no impurities are added; it corresponds to

$$PZ_0 = \frac{C_{Bf}}{k_cC_{c}C_{M}^{2}}$$

(5)

By substituting equation [5] into equation [4] and dividing by $C_{B0}$, the following expression is obtained:

$$PZ = \frac{1}{PZ_0} + \sum_{j=1}^{n} K_j' C_{j}$$

(6)

where the parameter $K_j'$ is defined as

$$K_j' = \frac{k_jC_{j}^{2j}}{C_{Bf}}$$

(7)

**Experimental**

Different impurities have been added to a commercial $\varepsilon$-caprolactam (99%, Sigma-Aldrich).

The following commercially available impurities were purchased from Sigma-Aldrich: cyclohexylamine, hexylamine, aniline, $o$-toluidine, $p$-toluidine, $\varepsilon$-caprolactone, phenol, nitrobenzene, 2-heptylamine, cyclohexanol, cyclohexene, hexylamide, and cyclohexanone oxime. Impurities that were not commercially available were octahydrophenazine, methyl-$\beta$-valerolactam, cyclohexenone oxime, and azocyclohepten-2-one. The octahydrophenazine and methyl-$\beta$-valerolactam were synthesized using procedures described previously [11,16], whereas cyclohexenone oxime and azocyclohepten-2-one were synthesized by the following procedures.

**Synthesis of 2-Cyclohexenone Oxime and Azocyclohepten-2-one**

2-Cyclohexenone oxime (CHE-Ox) was prepared by oxidation of 2-cyclohexenone with hydroxylamine sulfate using a procedure similar to one previously detailed for cyclohexanone oxime [11]. The organic phase was extracted with chloroform (5×350 mL). The combined organic phases were dried with Na$_2$SO$_4$ and the solvent was evaporated in vacuo. A mixture of two stereoisomeric 2-cyclohexenone oximes [syn (30%) and anti (70%)] was obtained (70 g, 0.63 mol, 62%) and a portion of this mixture was recovered for the synthesis of the azocyclohepten-2-one by means of a Beckmann rearrangement (B. R.).

The B. R. of the synthesized 2-cyclohexenone oxime was performed in 96% sulfuric acid media. The anti stereoisomer did not react at this step; only the syn stereoisomer rearranges to the $\alpha$,$\beta$-unsaturated lactam. These findings were confirmed by GC/MS.

The B. R. of 2-cyclohexenone oxime to the azocyclohepten-2-one was performed in a semibatch operation. CHE-ox (20 g) was slowly added to 75 mL of H$_2$SO$_4$ (96%) in a 250-mL glass flask at a temperature of 15°C. After the addition was complete the mixture was thermostatted at 75°C and the 250-mL flask was closed to increase the SO$_3$ content. The reaction was maintained for 72 h at 75°C until the syn oxime was reacted quantitatively (confirmed by GC/MS analysis). The flask was then cooled to room temperature and the reaction media was neutralized with NH$_3$ (30% v/v) at a temperature of 15°C. The organic phase was extracted with chloroform (3×100 mL). The combined organic phases were dried with MgSO$_4$, the solvent was evaporated under vacuum and the residue containing azocyclohepten-2-one was purified by column chromatography (silica gel; chloroform/ether, 2:1) Azocyclohepten-2-one was obtained as a yellow syrup (35%, 38.9 g).
Table 1. Impurities Added to Commercial ε-Caprolactam. PZ$_{0}$ = 22500 s

<table>
<thead>
<tr>
<th>Impurity (I)</th>
<th>Acronym</th>
<th>C$_i$ (mg/kg ε-caprolactam)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>ANL</td>
<td>2-10</td>
</tr>
<tr>
<td>α-Toluidine</td>
<td>αTOL</td>
<td>2-10</td>
</tr>
<tr>
<td>p-Toluidine</td>
<td>pTOL</td>
<td>1-10</td>
</tr>
<tr>
<td>Azocyclohepten-2-one</td>
<td>CLEN</td>
<td>1-100</td>
</tr>
<tr>
<td>2-Cyclohexenone oxime</td>
<td>CHE-OX</td>
<td>1-200</td>
</tr>
<tr>
<td>Cyclohexanone oxime</td>
<td>CHN-OX</td>
<td>10-1000</td>
</tr>
<tr>
<td>Phenol</td>
<td>PhOH</td>
<td>10-500</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>CHE</td>
<td>5-250</td>
</tr>
<tr>
<td>Octahydrophenazine</td>
<td>OHP</td>
<td>50-1000</td>
</tr>
<tr>
<td>ε-Caprolactone</td>
<td>CLN</td>
<td>10-2000</td>
</tr>
<tr>
<td>Methyl-δ-valerolactam</td>
<td>Me-VLM</td>
<td>100-3000</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>NBZ</td>
<td>500-100000</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>CHL</td>
<td>1000-100000</td>
</tr>
<tr>
<td>Hexanamide</td>
<td>HXM</td>
<td>100-10000</td>
</tr>
<tr>
<td>2-Heptylamine</td>
<td>HPA</td>
<td>1000-12000</td>
</tr>
<tr>
<td>Hexylamine</td>
<td>HX</td>
<td>500-5000</td>
</tr>
<tr>
<td>Cyclohexylamine</td>
<td>CHA</td>
<td>500-100000</td>
</tr>
</tbody>
</table>

Analytical Methods

The impurities synthesized in this work were analyzed by using a DB1 J&SCIENTIC column. Analysis conditions: carrier gas, helium, 1 mL/min; $T_{inj}$, 290°C; $T_{det}$, 230°C; split 25, 1:1; oven temperature, $T_0$ = 100°C; rate, 10°C/min; $T_1$ = 280°C, 1 min. The injection volume was 1 μL.

The protocol for the PZ determination was as follows: ε-caprolactam (3 g) containing a fixed amount of an impurity was dissolved in 100 mL of ultrapure distilled water. An aqueous solution of potassium permanganate (0.002 M, 1 mL) was added with agitation. The time required, PZ, to reach the same color as that of the reference solution (3 g of Co(NO$_3$)$_2$ + 12 mg of K$_2$Cr$_2$O$_7$ in 1 L of water) was measured (in seconds). Thus, the value of PZ is the time required for the oxidizable impurities in ε-caprolactam to reduce a fixed amount of KMnO$_4$. The procedure has been described previously in the literature (31).

Results and Discussion

Kinetic Equation for the Oxidation of the Impurities by Permanganate

The PZ number of a commercial ε-caprolactam was measured by the procedure described above; a value of 22500 seconds was obtained (PZ$_{0}$). Some impurities were added in different amounts to the ε-caprolactam; their concentrations are summarized in Table 1, and the corresponding PZ values were measured.

The decreases in the values of PZ as a function of the impurity concentrations are plotted in Figures 1 to 6. As can be seen in Figure 1, the impurities yielding the highest PZ decrease, even at concentration as low as 10 ppm, are aniline and both ortho- and para-toluidine.

The significant effects that the presence of cyclohexenone oxime, azocyclohepten-2-one, cyclohexanone oxime, phenol, and cyclohexene have on the PZ number are evident from the results presented in Figures 2 and 3. Thus, unsaturated and aromatic compounds with or without donor groups are easily oxidized by permanganate.

This finding can be attributed to the reaction between the permanganate ion and an aromatic ring or a carbon-carbon double bond, akin to an electrophilic addition, resulting in an activated five-membered cyclic manganese complex in its transition state [32]. Based on the concept of electrophilic addition, an increase of electron availability at the carbon-carbon double bond or aromatic ring should enhance the rate of the electrophilic addition reaction and, thus, the feasibility of the oxidation. This increase can be due to an amino or hydroxyl group as an electron-donor.
Although nitrobenzene is an aromatic compound, it is hardly oxidized (Figure 5) because it is functionalized with electron-attracting groups, a nitro group, that induces a deficiency of electrons at the aromatic ring. This deficiency of electrons reduces the rate of electrophilic attack on nitrobenzene.

We found that concentrations higher than 250 ppm are required for octahydrophenazine, $\delta$-valerolactam, $\varepsilon$-caprolactone, nitrobenzene, cyclohexanol, hexanamide, heptylamine, hexylamine, and cyclohexylamine to decrease the value of $PZ$ to half its initial value (Figures 4 to 6). The impurities that have a lower effect on the $PZ$ number are hexanamide, heptylamine, hexylamine, and cyclohexylamine. Therefore, we conclude that alkane impurities cause a small decrease in the permanganate number. The oxidation by permanganate of functionalized alkanes is based on a dual mechanism of electron transfer and hydrogen abstraction of the $\alpha$-carbon atom adjacent to the heteroatom, but the details are still an open question. The oxidation rate is limited by the rate of hydrogen atom abstraction from the $\alpha$-carbon.

The experimental $PZ$ values obtained at different concentrations of each impurity ($j$) have been fitted to equation [6] by a nonlinear regression [33] and the kinetic parameters $K_j$ and $p_j$ have been obtained. The reaction order, $p_j$, calculated for each impurity was rounded to the closest whole or fractional number and the experimental $PZ$ values were fitted again to equation [6], with the $p_j$ parameters set, to obtain the values of $K_j$. The nonlinear regression also provides an estimated $PZ$ value that should fit adequately the experimental one. The results we obtained are shown in Table 2.

Predicted $PZ$ values for each impurity were calculated by introducing, in equation [6], the corresponding kinetic parameters that are summarized in Table 2. Simulated values are plotted as lines in Figures 1 to 6. It can be seen that an excellent agreement is obtained between the experimental and predicted values, even when the impurity is added at a low concentration. Hence, this fact validates the hypothesis of a differential change in the concentrations of both reactants (permanganate and impurity) deduced from equation [6].

As can be seen from the results presented in Table 2, the reaction order varies from 0.5 to 2 depending on the nature of the impurity. Different values of the reaction order also have been reported in literature for the oxidation kinetics of several organic compounds by permanganate. Often, second-order overall, and first-order with respect to permanganate and the organic compound, rate constants have been found [23-28,30,34-39], but there are some papers showing both fractional-order, lower than...
Table 2. Parameters Calculated by Fitting of the Experimental PZ Values to Equation [6]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$PZ_0$ (_{\text{predicted}})</th>
<th>$K_i$</th>
<th>$p$</th>
<th>$SQR$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>22457</td>
<td>1.7E-5 ± 2.235E-6</td>
<td>2</td>
<td>509008</td>
</tr>
<tr>
<td>(\alpha)-Toluidine</td>
<td>23079</td>
<td>3.209E-6 ± 3.588E-7</td>
<td>2</td>
<td>1134546</td>
</tr>
<tr>
<td>(p)-Toluidine</td>
<td>22619</td>
<td>7.207E-6 ± 5.532E-7</td>
<td>2</td>
<td>435765</td>
</tr>
<tr>
<td>Azocyclohepten-2-one</td>
<td>22371</td>
<td>1.509E-5 ± 2.312E-6</td>
<td>1</td>
<td>1453540</td>
</tr>
<tr>
<td>Cyclohexenone oxime</td>
<td>22497</td>
<td>3.327E-5 ± 1.0388E-6</td>
<td>2</td>
<td>26661</td>
</tr>
<tr>
<td>Cyclohexanone oxime</td>
<td>21829</td>
<td>1.733E-6 ± 4.06E-7</td>
<td>1</td>
<td>3039978</td>
</tr>
<tr>
<td>Phenol</td>
<td>21664</td>
<td>2.792E-6 ± 2.635E-7</td>
<td>1</td>
<td>647545</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>20416</td>
<td>7.749E-8 ± 1.537E-8</td>
<td>2</td>
<td>2375854</td>
</tr>
<tr>
<td>Octahydrophenazine</td>
<td>22543</td>
<td>4.5E-6 ± 2.136E-7</td>
<td>0.5</td>
<td>298277</td>
</tr>
<tr>
<td>Caprolactone</td>
<td>22878</td>
<td>1.6506E-6 ± 1.031E-7</td>
<td>0.5</td>
<td>545992</td>
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<tr>
<td>Valerolactam</td>
<td>22017</td>
<td>2.565E-11 ± 2.986E-12</td>
<td>2</td>
<td>1215194</td>
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<tr>
<td>Nitrobenzene</td>
<td>23535</td>
<td>9.222E-7 ± 2.023E-9</td>
<td>0.5</td>
<td>954080</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>21706</td>
<td>4.695E-12 ± 3.343E-13</td>
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<td>311977</td>
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<tr>
<td>Hexanamide</td>
<td>23299</td>
<td>2.102E-7 ± 2.243E-8</td>
<td>0.5</td>
<td>467361</td>
</tr>
<tr>
<td>Heptylamine</td>
<td>21930</td>
<td>3.459E-10 ± 3.03E-13</td>
<td>2</td>
<td>592510</td>
</tr>
<tr>
<td>Hexylamine</td>
<td>22686</td>
<td>8.616E-12 ± 7.74E-13</td>
<td>2</td>
<td>741124</td>
</tr>
<tr>
<td>Cyclohexylamine</td>
<td>20576</td>
<td>1.37E-11 ± 1.948E-12</td>
<td>2</td>
<td>1553068</td>
</tr>
</tbody>
</table>

Table 3. Comparison Between Experimental PZ Values of Impurity Mixtures with Calculated PZ Values Obtained Using Equation [6]

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Impurity 1</th>
<th>Amount (ppm)</th>
<th>Impurity 2</th>
<th>Amount (ppm)</th>
<th>PZ Experimental</th>
<th>Calculated PZ</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CHN-Ox</td>
<td>12.5</td>
<td>HPA</td>
<td>750</td>
<td>16543</td>
<td>15088</td>
<td>8.79</td>
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<tr>
<td>2</td>
<td>CHN-Ox</td>
<td>25</td>
<td>HPA</td>
<td>1500</td>
<td>13021</td>
<td>11305</td>
<td>13.17</td>
</tr>
<tr>
<td>3</td>
<td>CHN-Ox</td>
<td>50</td>
<td>HPA</td>
<td>3000</td>
<td>7804</td>
<td>7472</td>
<td>4.24</td>
</tr>
<tr>
<td>4</td>
<td>CHN-Ox</td>
<td>12.5</td>
<td>ANL</td>
<td>0.25</td>
<td>14210</td>
<td>15095</td>
<td>-6.22</td>
</tr>
<tr>
<td>5</td>
<td>CHN-Ox</td>
<td>25</td>
<td>ANL</td>
<td>0.5</td>
<td>11842</td>
<td>11321</td>
<td>4.39</td>
</tr>
<tr>
<td>6</td>
<td>CHN-Ox</td>
<td>50</td>
<td>ANL</td>
<td>1</td>
<td>9173</td>
<td>7500</td>
<td>18.23</td>
</tr>
<tr>
<td>7</td>
<td>HPA</td>
<td>750</td>
<td>ANL</td>
<td>0.25</td>
<td>22011</td>
<td>22344</td>
<td>-1.51</td>
</tr>
<tr>
<td>8</td>
<td>HPA</td>
<td>1500</td>
<td>ANL</td>
<td>0.5</td>
<td>21315</td>
<td>21889</td>
<td>-2.69</td>
</tr>
<tr>
<td>9</td>
<td>(\alpha)TOL</td>
<td>3</td>
<td>ANL</td>
<td>1</td>
<td>6900</td>
<td>7873</td>
<td>-14.1</td>
</tr>
<tr>
<td>10</td>
<td>CHN-Ox</td>
<td>50</td>
<td>PhOH</td>
<td>20</td>
<td>5921</td>
<td>5349</td>
<td>9.6</td>
</tr>
<tr>
<td>11</td>
<td>CHL</td>
<td>3000</td>
<td>HPA</td>
<td>3000</td>
<td>10182</td>
<td>11182</td>
<td>-9.8</td>
</tr>
</tbody>
</table>

1 % Error = \(\frac{(PZ_{\text{Experimental}} - PZ_{\text{Calculated}})}{PZ_{\text{Experimental}}} \times 100\)

Figure 6. Effect of heptylamine, hexylamine and cyclohexylamine on the PZ value. Experimental (symbols) and predicted (lines) values with the kinetics parameters in Table 2.

These results were obtained using the PZ value of the original \(\varepsilon\)-caprolactam \((PZ_0 = 22500)\) and corresponding kinetic parameters in Table 3. Mixtures were prepared to contain impurities having both major and minor effects on the PZ value. The composition of these mixtures was varied to study the effect of impurity levels on PZ. The kinetic parameters were determined using the least squares method. The PZ values were calculated using Equation [6] and compared with the experimental PZ values. The results showed that the predicted PZ values were in good agreement with the experimental values, indicating the validity of the kinetic model. The PZ values were found to increase with an increase in the concentration of the impurities, which is consistent with the kinetic model predictions.

![Graph showing the effect of heptylamine, hexylamine and cyclohexylamine on the PZ value](image)

Figure 6. Effect of heptylamine, hexylamine and cyclohexylamine on the PZ value. Experimental (symbols) and predicted (lines) values with the kinetics parameters in Table 2.

The kinetic model has been validated by comparing the predicted PZ values with the experimental PZ values. The validation showed that the predicted PZ values were in good agreement with the experimental values, indicating the validity of the kinetic model. The PZ values were found to increase with an increase in the concentration of the impurities, which is consistent with the kinetic model predictions.
mixtures is given in Table 3 along with the experimental and predicted PZ values for each experiment. As can be seen, the predicted PZ values fit the experimental ones quite well; the highest percentage difference is lower than 20%.

**Conclusions**

We have found that aniline, ortho- and para-toluidine, cyclohexenone oxime, and azocyclohepten-2-one are impurities that cause the most dramatic decrease in the PZ number of ε-caprolactam. While the negative effects of aniline and ortho- and para-toluidine on the ε-caprolactam quality has been mentioned in the literature previously [7,17] the influences of cyclohexenone oxime and azocyclohepten-2-one have not been considered previously. However, they are common impurities in ε-caprolactam because they are produced by oximation and Beckmann rearrangement of the cyclohexenone obtained as an impurity in the cyclohexanol dehydrogenation. Because these latter two impurities are not commercially available, they were synthesized in this study.

Other impurities, such as hexanamide, heptylamine, hexylamine, and cyclohexylamine, have a small influence on the PZ number.

The capability for oxidation by permanganate ions depends on the type of organic compound. The oxidation reaction seems to proceed through the formation of intermediate complexes with manganese ions followed by decomposition of these complexes at the final stage.

The parallel scheme proposed includes the oxidation reactions between permanganate and each single impurity. An integrated equation has been developed from this scheme under the hypothesis of differential changes occurring to the concentration of both the reactant, permanganate, and impurities until the time PZ. This postulate has been validated by the good agreement obtained between the experimental and simulated PZ values, the latter calculated under this assumption. Kinetic constants and reaction orders obtained for the reactions involved in the parallel scheme that we have proposed provide helpful information useful for the analysis of the purification step.

**Nomenclature**

- $K_j$: Parameter defined in equation [6]
- $M$: Permanganate
- $p$: Reaction order for caprolactam or impurity
- $PZ$: Permanganate number
- $PZ_o$: Permanganate number of caprolactam before the addition of impurities
- $R$: Oxidized product
- $r$: Reaction rate
- $SQR$: Residual sum of squares
- $z$: Reaction order for permanganate

**Subscripts**

- $c$: Related to caprolactam
- $f$: Related to time to achieve the PZ
- $j$: Related to the impurity j
- $N$: Number of identified impurities on caprolactam
- $o$: Related to the initial value

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**References**

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