The Application of Buckingham π Theorem to Modeling Polypyrrole Synthesis done by Chemical Oxidative Polymerization

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Abstract
Buckingham π theorem was applied to model polypyrrole synthesis done by inverse emulsion polymerization route using Methanesulfonic acid as a dopant and potassium persulfate as an oxidant. A list of independent parameters on which polymerization depends was selected and by means of Buckingham theorem a functional relation between three dimensionless quantities; percent yield, conductivity and temperature was obtained. The actual form of the function was determined on the basis of experimental analysis and linear regression analysis. The accuracy of the proposed application was scrutinized by synthesizing pristine polypyrrole salt by the said polymerization route. It was corroborated from the experiment that the increase in percent yield and conductivity was directly proportional to the increase in oxidant concentration. Conductivity as high as 3.77 S/cm was obtained with a maximum percent yield of 94.54% at a moderate temperature range (293 K-298 K).

Keywords: Buckingham Pi Theorem, Chemical Oxidative Polymerization, Dimensionless Quantities, Mathematical Modeling, Polypyrrole, Regression Analysis

1. Introduction
Fused five membered ring systems and their analogs coupled with heterocycles are of great interest nowadays due to their intriguing electronic and biological applications, like solar cells, photoresists, nonlinear optical devices, synthetic biological tissues, transistors and electrical conductors¹⁴. Different heterocyclic compounds are converted into conducting polymers with the ability to display semiconducting properties when doped⁶. Polypyrrole is one such conducting polymer which has been comprehensively investigated due to its myriad properties like air stability and having a low band gap. In spite of being intractable, i.e. difficult to manage or control, this polymer is quite stable. The stability is the result of lone-pair of electrons on the nitrogen atoms which stabilize the positive charge in these p-doped polymers⁸. The chemical oxidative polymerization of pyrrole is a facile synthesis route for producing polypyrrole on a large scale⁶. The emulsion polymerization process has several distinct advantages. The physical state of the emulsion system makes it easier to control the process. Thermal and viscosity problems are much less significant than in bulk polymerization and the product obtained in many instances can be used directly without further separations¹⁰. A high reaction rate can be achieved by this technique. Emulsion polymerization is a unique process in that it affords the means of increasing the polymer molecular weight without decreasing the

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polymerization rate. In recent years, micro-emulsion polymerization and inverse emulsion polymerization techniques have attained significance in the preparation of polypyrrole. In this process, solution of a hydrophilic monomer is emulsified in a non-polar organic solvent and polymerization is initiated with an oil-soluble initiator. Inverse emulsion polymerization is used in various commercial polymerizations and co-polymerizations as well as water soluble monomers.

In this paper, synthesis of polypyrrole is modeled by applying Buckingham π theorem using inverse emulsion polymerization technique. Different polymerization reaction process parameters were studied and a list of independent parameters on which the polymerization process depended, were chosen on the basis of Buckingham π theorem. The actual model was corroborated by running the pilot experiment. Two different models were formulated; the percent yield model of polypyrrole and the conductivity model of polypyrrole based on the different percentage yields and conductivities obtained.

The π theorem as it is usually called is an important theorem in dimensional analysis which states that if there is a physically significant equation involving a certain number, $n$, of physical variables and $k$ is the rank of the dimensional matrix, then the original expression is equivalent to an equation involving a set of $p = n-k$ dimensionless parameters constructed from original variables. This theorem provides a method for computing sets of dimensionless parameters from the given variables, even if the form of the equation is still unknown.

Mathematically, the theorem can be expressed in the following form:

If $q_1$, $q_2$, $q_3$, ..., $q_n$ are $n$ dimensional variables that are physically relevant in a given problem and if they are interrelated by an unknown dimensionally homogenous set of equations then they can be expressed by the functional relationship,

$$F = (q_1, q_2, q_3, ..., q_n) = 0$$

(1)

If $n$ is the number of fundamental dimensions required to describe the $k$ variables, then there could be $n$ primary variables and the remaining $j = n-k$ variables that can be expressed as $(n-k)$ dimensionless and independent quantities called “π” groups, $π_1, π_2, π_3, ..., π_{n-k}$. Hence, the functional relationship can be reduced to a much more compact form as:

$$Φ (π_1, π_2, π_3, ..., π_{n-k}) = 0$$

(2)

where, $Φ$ = functional co-efficient of the “π” groups.

In the research presented herein, different polymerization process parameters were investigated to “set” perfect polymerization conditions and a mathematical model was formulated, further, a functional relationship between three dimensionless quantities; percentage yields of the polypyrrole salt synthesized, its conductivities and reaction temperatures was established.

The validity of the constructed mathematical model was confirmed by the actual synthesis of polypyrrole salt by the inverse emulsion polymerization route. In order to construct a mathematical model based on Buckingham π theorem, some rules need to be considered while formulating the actual model.

### 1.1 The Rules

- Write down the dimensions for all variables $A \ldots F$.
- Select $n$ of the variables - say $A$, $B$, $C$. These are called the repeating variables and will appear in all the $Π$ terms. However, there are certain restrictions:
  - None of the repeating variables can be dimensionless.
  - No two repeating variables can have the same overall dimension. For instance, $D$, the pipe diameter, and $r$, the roughness height, both have dimension of $L$ and so cannot both be used as repeating variables.
- Select one other variable - say $D$. Some combination of $A$, $B$, $C$, $D$ is dimensionless and forms the first $Π$ term or dimensionless group. We can find the combination by dimensional analysis, by writing the group in the form:

$$Π_1 = A^a B^b C^c D^d, \text{ so } [] = [A]^a [B]^b [C]^c [D]^d$$

Equating coefficients gives 3 equations for 4 unknowns, so we can express all the coefficients in terms of just one.

- Repeat this procedure with the repeating variables and the next variable, so use $A$, $B$, $C$, $E$. Continue until no variables are left.
- Having worked out all the dimensionless groups, the relationship between the variables can be expressed as a relationship between the various groups. Typically we can write this as one group (for example $Π_1$) as a function of the others:

$$Π_1 = f(Π_2, Π_3, \ldots)$$

Based upon these set of rules the percentage yield model and the conductivity model for polypyrrole was constructed.
2. Experimental Part

2.1 Mathematical Modeling of Polypyrrole Synthesis based on Buckingham π Theorem

Following steps were followed according to Buckingham π theorem to construct the mathematical model:

2.1.1 Choosing Independent Variables or Parameters that directly Affected the Experimental Results and their Designations

Influence of process parameters on the polymerization of pyrrole monomer were studied to optimize the synthesis conditions and “set” the perfect synthesis conditions. During polypyrrole synthesis following process parameters were studied and they were designated as:

- Monomer Concentration (ml) \( M \)
- Surfactant Concentration (g) \( S \)
- Oxidant Concentration (g) \( O \)
- Dopant Concentration (ml) \( D \)
- Revolutions per Minute \( R \)
- Stirring Time (min.) \( S_t \)
- Temperature (\( \theta \)) \( T \)

Hence, total number of independent variables that were identified, \( n = 7 \) (Primary variables)

Therefore, according to Equation (2),

\[
F = (M, S, O, D, R, S_t, \theta) = 0
\]

(3)

2.1.2 Choosing the “Repeating Variables” which Appear in all the \( \pi \) Terms and not having the same Overall Dimensions

They were classified as:

- Monomer Concentration (ml) \( M \)
- Surfactant Concentration (g) \( S \)
- Temperature (\( \theta \)) \( T \)

2.1.3 Counting the Actual Number of Dimensions that are Considered for the Experiment

Surfactant and oxidant concentrations are usually expressed in grams (g), i.e. Mass (M)

Monomer and dopant concentrations are usually expressed in milliliters (ml), i.e. Volume (V)

Stirring time is usually expressed in minutes (min), i.e. Time (T)

Revolutions per Minute (RPM) of the stirrer is expressed as Frequency (F) and \( \theta \) is the Temperature (T)------ Already a dimensionless parameter, hence a separate \( \pi \) factor.

Hence total number of variables identified were \( k = 4 \)

Therefore, total \( \pi \) groups identified can be calculated as, \( j = n - k \) i.e. \( j = 7 - 4 = 3 \) i.e. Percentage Yield, Conductivity and temperature were identified as dimensionless parameters.

2.1.4 Formulation of the Actual \( \Pi \) Terms

Synthesis of polypyrrole was found to depend upon the following listed process parameters. Writing them down and classifying them along with their dimensions in M (Mass) and T (Time) terms:

| Process Parameter | Dimension (M or T) |
|------------------|--------------------|
| Monomer Concentration | ml |
| Surfactant Concentration | g |
| Oxidant Concentration | g |
| Dopant Concentration | ml |
| Revolutions per Minute | RPM |
| Stirring Time | min |
| Temperature | \( \theta \) |

Choosing Monomer (M), Surfactant (S), Oxidant (O) and Dopant (D) as “repeating” units, the first dimensionless quantity \( \pi_1 \) takes the form,

\[
\Pi_1 = [M]^a[S]^b[O]^c[D]^d[ml]^e[g]^f[g]^g[ml]^h
\]

Since, 1 gm = 10\(^{-3}\) Kg and 1 ml = 10\(^{-3}\) L in SI units, This gives the relation:

\[
0 = a - b \text{ or } a = b \quad (4)
\]

\[
0 = c - d \text{ or } c = d \quad (5)
\]

A Revolution per Minute (RPM) is a measure of the Frequency (F) of a rotation and is expressed as r.min\(^{-1}\) in SI units whereas stirring time (\( S_t \)) is expressed in minutes.

Choosing RPM and \( S_t \) as “repeating” units, the second dimensionless quantity \( \pi_2 \) takes the form:

\[
\Pi_2 = [F]^e[T]^f = [min^{-1}]^e[\text{min}]^f
\]

This gives the relation:

\[
0 = -e + f \text{ or } e = f \quad (6)
\]

or

\[
e = -f \quad (7)
\]

Substituting the value of \( e \) from (7) in (6), we get,

\[
0 = -f + f \text{ or } e = f \quad (8)
\]
According to Buckingham pi theorem, if a quantity is dimensionless it is considered as a separate π term. Hence, temperature (θ) can be considered as a separate π factor.

\[ \Pi_1 = \text{Temperature} (\theta) = 20^\circ C \]

Also, according to Buckingham pi theorem if any two parameters are having the same dimensions, their ratio is a π term. Hence, the above equations confirm the calculation of the π terms.

All the reactions were carried out using standard laboratory apparatus unless otherwise noted. Pyrrole monomer (Acros) 99.9% extra pure, organic reagents like chloroform (Fischer Scientific) (99.9% extra pure), acetone (Fischer Scientific) (Analar grade, 99% pure), dopant methane sulfonic acid and surfactant sodium lauryl sulfate (Procured from National Chemicals, India) along with oxidant potassium persulfate (Procured from Qualigens Fine Chemicals, India) were used as received.

Resistance measurement of polypyrrole was carried out on a two probe connected to a Mastech digital multimeter (Model MAS 830L). Regression graphs were plotted using the standard Microsoft Excel software.

2.2 Polymerization Procedure

2.2.1 Preparation of Polypyrrole Salt using Methane Sulfonic Acid as a Dopant

In a 250ml conical flask was stirred a mixture of methane sulfonic acid dopant (4ml, 5.92g) and water (20ml). Pyrrole monomer (1.2ml, 1.16g) dispersed in water (30ml) was added to the above mixture and constantly stirred at 293 K. Sodium lauryl sulfonate surfactant (1.0g) dispersed in water (20ml) and Potassium persulfate initiator (3.0g) dispersed in Chloroform (30ml) were added dropwise to the stirring reaction mixture. The reaction mixture was allowed to stir constantly for one hour duration, after which it was poured in acetone to precipitate the black colored polymer. The polymer was washed with water, dried in an oven at 383 K and weighed until a constant weight was maintained.

3. Results and Discussion

Table 1 summarizes the percent yield model. It is seen that by varying the oxidant concentration the actual experimental data and the pi model coincide, (% yield- pi exp. 94.54% and pi model 93.81%). The table suggests that for “set” concentrations of monomer, surfactant, dopant, RPM, stirring time and temperature, varying the oxidant concentrations significantly increases the percent yield of polypyrrole salt. Figure 1 A comparison between yield experiment and yield model gives an idea how the yield experiment graph and the model graph coincide.

Linear regression analysis (goodness of fit) of the first four points gives the \( R^2 \) value 0.853, which very well confirms that the experimental data fits the statistical model. Goodness of fit of the last three points gives the \( R^2 \) value 0.931 which confirms that the yield experiment coincides with the yield model. Figure 2 Linear Regression Analysis (probability) for first four points and Figure 3 Linear Regression Analysis (Probability) of the last three points corroborates these findings.

However, a sudden increase in conductivity was observed in the conductivity experiment. Table 2 summarizes the conductivity model. The table suggests that by varying the oxidant concentration till 5.25 g conductivity steadily increases (3.25 S•cm\(^{-1}\)), however slight increase in oxidant concentration to 5.5 g increases conductivity to 3.77 S•cm\(^{-1}\). Figure 4 Conductivity experiment (actual). Figure 5 A comparison between conductivity experiment

Table 1. The Percent Yield Model.

| Monomer Conc (ml) (1) | Surfactant Conc (g) (2) | Oxidant Conc (g) (3) | Dopant Conc (ml) (4) | RPM (5) | Temp (6) | Stirring Time (min) (7) | % yield (pi exp) | (pi 1) | (pi 2) | (pi 3) | \( n_1 + n_2 + n_3 \) | pi (model) |
|----------------------|------------------------|----------------------|---------------------|--------|---------|------------------------|-----------------|--------|--------|--------|-----------------|-----------|
| 1.2                  | 1                      | 1.75                 | 4                   | 300    | 20      | 60                     | 19.04           | 5.833333333 | 18000  | 20     | 2100000         | 5.283     |
| 1.2                  | 1                      | 2                    | 4                   | 300    | 20      | 60                     | 21.14           | 6.666666667 | 18000  | 20     | 2400000         | 17.283    |
| 1.2                  | 1                      | 2.5                  | 4                   | 300    | 20      | 60                     | 40.28           | 8.333333333 | 18000  | 20     | 3000000         | 41.283    |
| 1.2                  | 1                      | 2.75                 | 4                   | 300    | 20      | 60                     | 74.76           | 9.166666667 | 18000  | 20     | 3300000         | 53.283    |
| 1.2                  | 1                      | 3                    | 4                   | 300    | 20      | 60                     | 83.77           | 10          | 18000  | 20     | 3600000         | 83.018    |
| 1.2                  | 1                      | 3.5                  | 4                   | 300    | 20      | 60                     | 86.63           | 11.66666667 | 18000  | 20     | 4200000         | 88.418    |
| 1.2                  | 1                      | 4                    | 4                   | 300    | 20      | 60                     | 94.54           | 13.33333333 | 18000  | 20     | 4800000         | 93.818    |
Figure 1. A comparison between yield experiment and yield model.

Figure 2. Linear Regression Analysis(Probability) for first four points.

Table 2. The Conductivity Model.

| Monomer Conc (ml) | Surfactant Conc (g) | Oxidant Conc (g) | Dopant Conc (ml) | RPM (5) | Temp (6) | Stirring Time (min) | Conductivity (pi exp) | pi 1 | pi 2 | pi 3 | pi n1=n2=n3 | pi (model) |
|------------------|---------------------|------------------|------------------|---------|----------|---------------------|-----------------------|------|------|------|-------------|-----------|
| 1.2              | 1                   | 1.5              | 4                | 300     | 20       | 60                  | 0.71                  | 5    | 1800000 | 0.704 |
| 1.2              | 1                   | 1.75             | 4                | 300     | 20       | 60                  | 0.72                  | 5.833333 | 1800000 | 0.713 |
| 1.2              | 1                   | 2                | 4                | 300     | 20       | 60                  | 0.87                  | 6.666667 | 1800000 | 0.8698 |
| 1.2              | 1                   | 2.5              | 4                | 300     | 20       | 60                  | 0.88                  | 8.333333 | 1800000 | 0.8758 |
| 1.2              | 1                   | 5                | 4                | 300     | 20       | 60                  | 0.91                  | 16.666667 | 1800000 | 0.9058 |
| 1.2              | 1                   | 5.25             | 4                | 300     | 20       | 60                  | 3.25                  | 17.5 | 1800000 | 4.93 |
| 1.2              | 1                   | 5.5              | 4                | 300     | 20       | 60                  | 3.77                  | 18.333333 | 1800000 | 5.33 |

Figure 3. Linear Regression Analysis(Probability) of the last three points.

Figure 4. Conductivity experiment (actual).
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and conductivity model shows that the conductivity (π experiment - 3.77 S•cm⁻¹) and the conductivity (π model - 5.53 S•cm⁻¹) do not coincide. The conductivity π model is shown in Figure 6 The Conductivity Model. Figure 7 Linear Regression Analysis (probability) for first two points gives the R² value of 1 which indicates that regression line perfectly fits the data. Figure 8 Linear Regression Analysis (probability) for the next three points gives the R² value of 0.992 and it is here at this point that slight deviation in conductivity towards higher side is observed, which can be attributed to the fact that a full conducting path is getting formed for the passage of current, which is confirmed from Figure 9 Linear Regression Analysis (probability) for the last two points when sudden increase in conductivity value is observed (i.e. from 3.25 S•cm⁻¹ to 3.77 S•cm⁻¹).

Figure 5. A comparison between conductivity experiment and conductivity model.

Figure 6. The Conductivity π Model.

Figure 7. Linear Regression Analysis (Probability) for first two points.

Figure 8. Linear Regression Analysis (Probability) for the next three points.

Figure 9. Linear Regression Analysis (Probability) for the last two points.
This sudden increase in conductivity can be explained on the basis of Percolation Theory which predicts that at a certain amount of polypyrrole a full conducting path is formed for the flow of current beyond a point called percolation threshold, which is a critical point at which the particles of the polymer exist as giant clusters which facilitate the flow of current and conductivity arises. Below this percolation threshold there is no significant conductivity since particles do not form clusters. Figure 10 SEM Micrograph of polypyrrole at 1500 X magnification clearly indicates the occurrence of polypyrrole as giant clusters.

4. Conclusions

Buckingham pi theorem was successfully employed to model polypyrrole synthesis done by inverse emulsion polymerization. A functional relationship between three dimensionless quantities; percent yield, conductivity and temperature was established. The model was verified by the actual synthesis of the polymer. A sudden increase in conductivity was explained on the basis of percolation theory and justification was aptly given as to why the yield experiment and yield model coincides whereas the conductivity experiment and the conductivity model don’t. Conductivity as high as 3.77 S·cm⁻¹ was obtained at 20°C temperature with a relatively high percent yield of 94.54%. It was confirmed from the experiment that the percent yield and conductivity was directly proportional to the increase in the oxidant concentration.

5. References

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