Chapter 4

Experimental procedures
Chapter FOUR

EXPERIMENTAL PROCEDURES

The aim of the present investigation is to obtain the ionic mass transfer and pressure drop data in three phase fluidized beds in the presence of disc promoter. In this chapter, the measurement of pertinent variables such as the limiting current, the pressure drop and bed porosities have been detailed. This chapter is divided into three sections. In the first section the method of measurement of limiting current and the calculation of mass transfer coefficient is mentioned. The measurement of pressure drops and evaluation of different phase holdups is presented in the second section. Precautions to be taken during experimentation are listed in the third section.

The chemicals used in the preparation and analysis of the electrolyte are listed in table 4.1 with their graded quality.

Table 4.1

Various chemicals used in the present study

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Grade</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen gas</td>
<td>AR</td>
<td>BOC</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>AR</td>
<td>BDH</td>
</tr>
<tr>
<td>Potassium dichromate</td>
<td>AR</td>
<td>BDH</td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>AR</td>
<td>BDH</td>
</tr>
<tr>
<td>Potassium ferrocyanide</td>
<td>AR</td>
<td>BDH</td>
</tr>
<tr>
<td>Potassium ferricyanide</td>
<td>AR</td>
<td>E.Merck</td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>GR</td>
<td>E.Merck</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>GR</td>
<td>Qualigens</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>Pure</td>
<td>Qualigens</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Excelar</td>
<td>Glaxo</td>
</tr>
<tr>
<td>Sodium thiosulphate</td>
<td>AR</td>
<td>Glaxo</td>
</tr>
<tr>
<td>Starch</td>
<td>Pure</td>
<td>Glaxo</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>AR</td>
<td>Sarabhai</td>
</tr>
</tbody>
</table>
The range of parameters covered in the present investigation are compiled in table S.1 (page no:xiii). The geometries of the different promoters employed are compiled in table 3.1 (page no: 140).

4.1. Measurement of limiting currents:

The measurement of limiting current was made at copper microelectrodes fixed flush with the inner surface of the test section (fig 3.2). These microelectrodes have the diameter of 0.0035 m. The system chosen for the measurement of limiting current is potassium ferricyanide - ferrocyanide couple. The limiting current can be measured using diffusion controlled electrode reaction, reduction of ferricyanide ion and oxidation of ferrocyanide ion. The electrode reactions involved in this study are:

\[
[\text{Fe(CN)}_6]^{3-} + e \rightarrow [\text{Fe(CN)}_6]^{4+} \quad \text{Reduction of ferricyanide ion ...(4.1)}
\]

\[
[\text{Fe(CN)}_6]^{4+} - e \rightarrow [\text{Fe(CN)}_6]^{3-} \quad \text{Oxidation of ferrocyanide ion ... (4.2)}
\]

This electrochemical system has been chosen because (i) the limiting current measurement is fast, accurate and reproducible, (ii) chemical polarization is negligible and (iii) the electrode surface remains smooth and uneffected.

Before starting the experimentation, the microelectrodes were polished with fine emery paper and cleaned thoroughly. The dimensions of the micro electrodes were measured accurately. The disc diameter, disc spacing, promoter rod diameter
and other relevant dimensions were accurately measured with Vernier calipers. The rotameters were pre-calibrated using water, before starting the experimentation.

100 L of distilled water of 5 μmho specification were taken in the storage tank. Potassium ferricyanide, potassium ferrocyanide and sodium hydroxide were added to the distilled water in calculated quantities in such a way that the resulting electrolyte contained 0.01 N potassium ferricyanide, 0.01 N potassium ferrocyanide and 0.5 N sodium hydroxide. This electrolyte was de-aerated using nitrogen. Sodium hydroxide was used as an indifferent electrolyte to carry the current. Initially blank runs were conducted with indifferent electrolyte alone. Since no appreciable currents were detected, it could be ascertained that the measured limiting currents during the redox reactions were only due to depolarizing agent. The disc promoter was fixed concentrically in the test section. The test section was charged with glass beads of known weight and uniform diameter. The electrolyte and nitrogen were circulated at desired velocities through the test section and the bed of solids was fluidized to desired height.

Measurement of limiting current was made in the lines similar to those reported earlier in the studies on ionic mass transfer [1,2]. The limiting current at any point electrode for the reduction of fericyanide ion was first measured by impressing an applied potential across the micro copper electrode (cathode) and wall of the copper column (anode) in small increments. The value of the limiting current was obtained from the plots drawn between current and applied potential. The attainment of the limiting current was indicated by negligible increase in current for considerable
increase in potential. This graphical method to obtain the limiting current, was illustrated in fig 4.1. From the measured limiting current value \( (i_L) \) at any given electrode, the mass transfer coefficient was calculated using the following equation.

\[
k_L = \frac{i_L}{zAFC_0}
\]  

...(4.3)

Where \( C_0 \) = concentration of the reaction ion in bulk solution, Kmols/m³

\( A \) = area of the electrode, m²

\( z \) = number of electrons participating in the reaction

\( F \) = Faraday constant, 96500 C / g .equivalent

\( k_L \) = mass transfer coefficient, m/s

Derivation of equation (4.3) is presented in detail in Appendix–A. The electrical circuit employed for the measurement of limiting currents was shown as fig 3.4.
During each run, the reacting ion concentration was obtained by volumetric analysis. The ferrocyanide ion concentration was estimated by permanganometric titration method and the ferricyanide ion concentration was obtained using iodometric titration method. Estimation of NaOH concentration was made by titrating the electrolyte against standard oxalic acid solution [4]. The temperature of the electrolyte for each run was measured upto ±0.1°C accuracy. The densities of the electrolyte were measured with a specific gravity bottle. Viscosities for each temperature condition were taken from the existing data [1]. The values of diffusivities for the conditions of each experimental run were calculated using Lin et al [1] equation.
4.2. Measurement of pressure drops:

Spherical glass beads of different diameters were used as bed materials in the present investigation. A representative sample consisting of known number of particles was subjected to water displacement method to determine the diameter and density of the particles. The particle diameter obtained by this method was also verified with a micro-meter. The test section was charged with particles of known weight. The electrolyte and nitrogen were circulated at desired velocities through the test section and the bed of solids was fluidized to desired height. The pressure drop between the two pressure taps was noted by connecting a U-tube manometer. The bed height was noted with a pre-fixed scale. The solids hold up was determined from bed height measurements [5,6].

Measurement of gas holdups was made from these pressure drop measurements [5-7]. The method of determining gas hold-up is as follows. Liquid at a desired flow rate is admitted into the test section. The gas was allowed through the sparger. Solid particles of known weight were charged to the test section. The bed was raised / fluidized up to the predetermined level corresponding to the pressure tapings at the top of the test section. A manometer fixed across the test section recorded the pressure drop ($\Delta P^*$) of the three-phase fluidized bed. The gas flow rate was stopped and the liquid velocity was increased such that the bed height was measured to the same predetermined level. The manometer reading for this case was $\Delta P'$, corresponding to the liquid fluidized bed. The following equation was used to compute gas hold up.
$$\varepsilon_s = \frac{\Delta P - \Delta P^*}{gH\rho_l} \quad \ldots (4.4)$$

The solids hold up was calculated using the relation.

$$\varepsilon_s = \frac{W_s}{\rho_sA_cH} \quad \ldots (4.5)$$

Since $\varepsilon_s + \varepsilon_L + \varepsilon_g = 1$,

liquid hold up was obtained as

$$\varepsilon_L = 1 - \varepsilon_s - \varepsilon_g \quad \ldots (4.6)$$

The bed porosity $\varepsilon$ was estimated as

$$\varepsilon = 1 - \varepsilon_s = \varepsilon_L + \varepsilon_g \quad \ldots (4.7)$$

4.3. Precautions:

The following precautions were taken during the experimentation

- The point electrodes were cleaned and polished at frequent intervals.
- The electrical connectivity of the electrodes was periodically checked.
- The data were tested for their reproducibility from time to time by repeating any one of the previous runs under identical conditions.
- If the temperature differed by $\pm 0.1^\circ C$ in any run, that individual run was rejected.
Nomenclature

A = area of the reacting surface $[\text{m}^2]$ 
\(A_c\) = cross-sectional area of test-section $[\text{m}^2]$ 
\(C_0\) = concentration of reacting ion (Fe\(^{2+}\) or Fe\(^{3+}\)) $[\text{kmol/m}^3]$ 
\(d_p\) = particle diameter $[\text{m}]$ 
E = applied potential $[\text{V}]$ 
F = Faraday constant $[\text{C}]$ 
g = acceleration due to gravity $[\text{m/s}^2]$ 
H = height of test-section $[\text{m}]$ 
i = current $[\text{A}]$ 
\(i_L\) = limiting current $[\text{A}]$ 
\(k_L\) = mass transfer coefficient $[\text{m/s}]$ 
\(U_g\) = superficial gas velocity $[\text{m/s}]$ 
\(U_L\) = superficial liquid velocity $[\text{m/s}]$ 
\(W_s\) = weight of solids $[\text{kg}]$ 
X = longitudinal distance $[\text{m}]$ 
z = number of electrons released or consumed during the reaction $[-]$
Greek Letters

$\Delta P^* = \text{pressure drop in liquid fluidized bed}$ [Pa]

$\Delta P^{**} = \text{pressure drop in three-phase fluidized bed}$ [Pa]

$\varepsilon = \text{bed porosity}$ [-]

$\varepsilon_g = \text{gas holdup in three phase fluidized bed}$ [-]

$\varepsilon_L = \text{liquid holdup in three phase fluidized bed}$ [-]

$\varepsilon_s = \text{solid holdup in three phase fluidized bed}$ [-]

$\rho_s = \text{density of solids}$ [kg/m$^3$]

$\rho_L = \text{density of liquid}$ [kg/m$^3$]
References


