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Chemical Reaction Engineering

II

Chemical Reaction Engineering II

Manual for Performing Laboratory Exercises

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Determination of Conversion of Sucrose in a Packed Bed Continuous Reactor

Purpose of the exercise

Sucrose hydrolysis, also known as sucrose inversion, is a first-order acid-catalyzed reaction that produces equimolar amounts of glucose and fructose:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

$$\quad A \qquad\qquad B \qquad\qquad\qquad C \qquad\qquad D$$
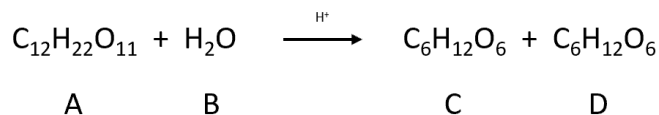
The purpose of this exercise is to study sucrose inversion in a packed bed catalytic reactor. In this type of reactor, the catalyst is immobilized into porous round particles of the carrier (support matrix), which are trapped in the reactor. The sucrose solution pumped into the reactor is mixed with the catalyst, which leads to the formation of the product. The advantage of using heterogeneous catalyst is that the separation of the catalyst from the product is not necessary, which is more advantageous from an economic point of view, and above all because of the practicality of conducting experiments. The sucrose inversion reaction will be carried out in a chemical reactor in the presence of a chemical catalyst Amberlite IR-120.

Theoretical background

Conversion

The conversion of sucrose, X_A, in a constant volume reactor is calculated:

$$X_A = 1 - \frac{c_A}{c_{A0}} \tag{1.1}$$

where: X_A conversion according to sucrose, c_{A0} initial concentration of sucrose, and c_A concentration of sucrose.

Kinetic model

It is known that this reaction is an irreversible reaction of the first order, so we can write:

$$- r_A = - \frac{dc_A}{dt} = k\, c_A \tag{1.2}$$

where: r_A eaction rate, c_A concentration of sucrose, t time and k reaction rate constant. The equation applies to discontinuous operation. If we replace the reaction time with the residence time in the equation for calculating the reaction rate (equation (1.2)), we get the equation that applies to flow reactors with a constant volume:

$$- r_A = - \frac{dc_A}{d\tau} = k\, c_A \tag{1.3}$$

where: τ residence time.

Using the integral method, the reaction rate constant can be determined from the slope of the line on a graph of $\ln\dfrac{c_{A0}}{c_A}$ versus residence time, τ :

$$\ln \frac{c_{A0}}{c_A} = k\, \tau \tag{1.4}$$

where: c_{A0} initial concentration of sucrose, c_A concentration of sucrose in the steady state, and τ residence time, calculated according to the mass of the catalytic, *m*:

$$\tau = \frac{m}{q_V} \tag{1.5}$$

where: q_V volume flow of the reaction solution through the reactor and *m* mass of the dry catalyst.

Activation energy

For the determination of the activation energy for selected reaction it is necessary that the reaction is carried out at least at three different temperatures. It is known that the temperature affects the reaction rate constant. Activation energy and pre-exponential factor are obtained from the Arrhenius equation:

$$k = k_0\, e^{-\frac{E_a}{RT}} \tag{1.6}$$

where: k_0 is the pre-exponential factor, R gas constant, T temperature and E_a activation energy.

Accessories and chemicals

- flasks,
- cation exchanger,
- sucrose,
- glucose,
- glucose reagent,
- Eppendorf tubes,
- cuvette,
- magnetic stirrer.

Experimental procedure

The conversion of sucrose is determined by measuring the concentration of produced glucose. To do this, prepare standard glucose solutions ($\gamma = (1, 2, 3, 4)$ g·L^{-1}), and sucrose solution with a concentration of $\gamma = 7.6$ g·L^{-1}.

The schematic diagram of the Armfield CEU laboratory reactor system, in which the sucrose inversion reaction will be performed, is shown in Figure 1.1.
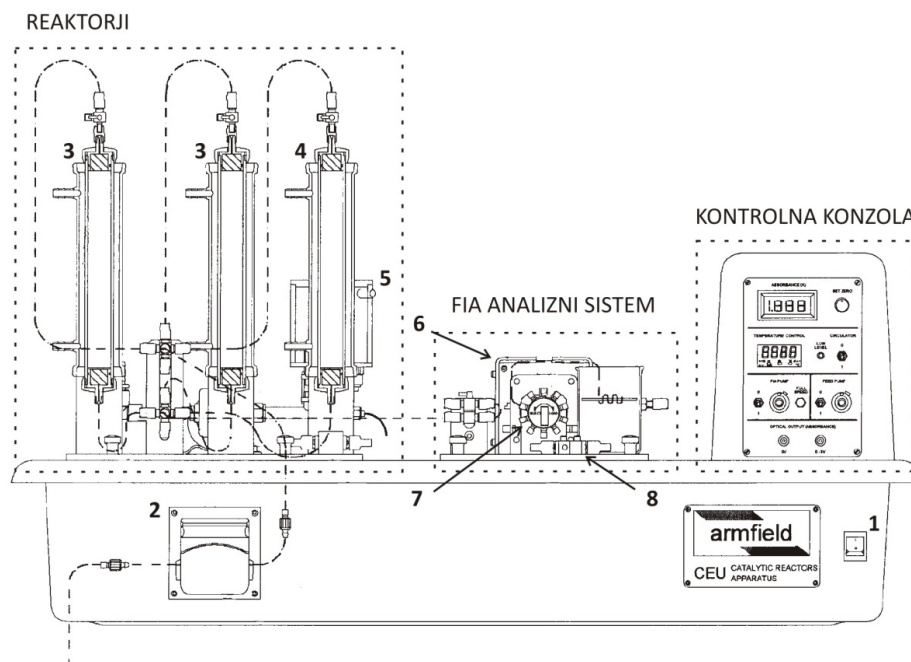
Figure 1.1: Armfield CEU laboratory reactor system (1 – on/off switch, 2 – peristaltic pump, 3 – chemical reactors, 4 – enzyme reactor, 5 – thermostar, 6 – FIA pump, 7 – FIA valve, 8 – flow optical cell).

Source: [image from Armfield CEU laboratory reactor system instruction manual]

The entire reactor system consists of three parts: the central part, which consists of three packed bed reactors (two chemical and one enzyme), the FIA analysis system and the control console.

The sucrose solution is pumped through the desired reactor by means of a peristaltic pump (2). Sucrose reacts in a reactor, and the product - glucose that is formed is analyzed with a spectrophotometer.

Chemical reactor

For the preparation of chemical reactors, use the cation exchanger Amberlit IR-120, which is pre-sieved. Two different particle sizes are used for the fixed bed. The fraction with an average particle size, $d = 0.86$ mm, is obtained using sieves with a pore size of 1 mm and 0.71 mm, the second fraction with an average particle size, $d = 0.31$ mm, is obtained by sieves with a pore size of 0.355 mm and 0.25 mm. Both reactors are filled with wetted particles.

Before starting the experiment, activate the catalyst by pumping 500 mL of $c = 2$ mol·L^{-1} hydrochloric acid through the reactor at a flow rate of $q_V = 10$ mL·min^{-1}. Then, during purging the catalyst with 500 mL of degassed distilled water, the reactor is heated to the desired temperature ($T = (45, 50, 55, 60, 65$ and $70)$ °C). Degassing the distilled water and the sucrose solution prevents the formation of air bubbles in the catalyst layer. The sucrose solution is pumped through the reactor with flow, $q_V = (6, 8$ in $10)$ mL·min^{-1}.

Analysis with a static optical cell

The concentration of produced glucose is determined by a static optical cell indirectly using a glucose reagent and measuring the absorbance of the dye formed when the glucose reagent reacts with glucose. Absorbance is measured at 510 nm. The glucose concentration is determined based on a calibration curve previously prepared by measuring the absorbances of glucose solutions of known concentrations.

Prepare 1 mL plastic cuvettes. Place 990 µL of glucose reagent in each Eppendorf tube. Then, at intervals of 30 s, add 10 µL of the sample or standard glucose solution to the tube. Close the tubes and mix well. Before measurement, pour the solution into cuvettes and measure the absorbance at 510 nm exactly 10 minutes after the addition of the sample or standard solution.

Experimental part

The fixed bed in the chemical reactor represents activated Amberlit IR-120. During purging the catalyst with 500 mL of degassed distilled water, the reactor is heated to the desired temperature (T = (45, 50, 55, 60, 65 and 70) °C). The sucrose solution is pumped through the reactor with a volume flow q_V = (6, 8 and 10) mL·min^{-1}.

With switch 1 (Figure 4.1) switch on the reactor system. Before the reaction begins, it is necessary to calibrate the peristaltic pump (2) with distilled water, which is later used to pump the sucrose solution through the reactor. When the pump is calibrated, the switch is set to the desired flow rate and while pumping the distilled water, start heating the jacketed reactor to the desired temperature.

Prepare 1 L of sucrose solution with the concentration γ = 7.6 g·L^{-1}. Pour the solution from the flask into a bottle. Put a magnetic stirrer in the bottle and start stirring. Once a steady state is reached, collect a few drops of the sample from the reactor outlet into Eppendorf tubes.

To determine the concentration of the resulting product, prepare 100 mL of each standard glucose solution with concentration of, γ = (1, 2, 3, 4) gL^{-1}, measure absorbance and plot a calibration curve.

Calculation and results

− plot calibration curve,
− create a table with the residence time (g·min·mL^{-1}), concentration of glucose and sucrose in steady state (mol·L^{-1}) and conversion at different temperatures,
− plot $\ln \frac{c_{A0}}{c_A}$ = f (τ) at all temperatures and from the slope of the line determine the reaction rate constants, which, depending on the temperature, are given in tabular form
− plot Arrhenius plot,
− calculate pre-exponential factor, k_0, and activation energy, E_a.

2. EXERCISE

Corrosion Resistance of Materials

Purpose of the exercise

Stainless steels are important materials in chemical, petroleum, and process industries. In the chemical processing industry, 50 % of the damage is caused by corrosion of stainless steels and the other half by mechanical damage. By selecting the appropriate material, corrosion can be minimized, but it is essential to understand its resistance under specific conditions. We need to answer the question of what the rate of corrosion will be and whether the material will corrode in an active or passive state. In most cases, the answer to these questions is given by the classic method, where we immerse the sample in the chosen medium, but this method is time-consuming. The electrochemical (potentiodynamic) method is faster. With this method, polarization curves are obtained, from which the corrosion characteristics of the metal or alloy in a given medium are obtained and the conditions for anode protection.

In the exercise, we also learn about contact corrosion with its characteristics and an example of a eutectic mixture at room temperature.

Theoretical background

Classic method

Corrosion rate, *r*, according to the classical method is calculated as the loss of mass of the material on a given surface:

$$r = \frac{\Delta m}{A\,t} \tag{2.1}$$

where: *t* exposure time, *A* surface area of the sample, and Δm mass loss calculated as:

$$\Delta m = m_0 - m \tag{2.2}$$

where: m_0 initial weight of the sample, and *m* mass of the sample after exposure to the corrosive medium.

The area of the metal sample (ring) is calculated:

$$A = \frac{\pi}{2}\,(D^2 - d^2) + b\,\pi\,D + b\,\pi\,d \tag{2.3}$$

where: *D* sample diameter, *d* diameter of the hole for the holder, *b* sample thickness.

Electrochemical method

The electrochemical method is used to determine the rate and the way of corrosion (total or local) and the conditions for anode protection. The basis of this method is the theory of mixed potentials, which was given in its modern form by Wagner and Traud. According to this theory, the total rate of all oxidation reactions is equal to the total rate of reduction reactions on the corroding surface. Oxidation takes place at the anode sites of the metal and the electrons released in this process are consumed during reduction on the cathode parts of the metal.
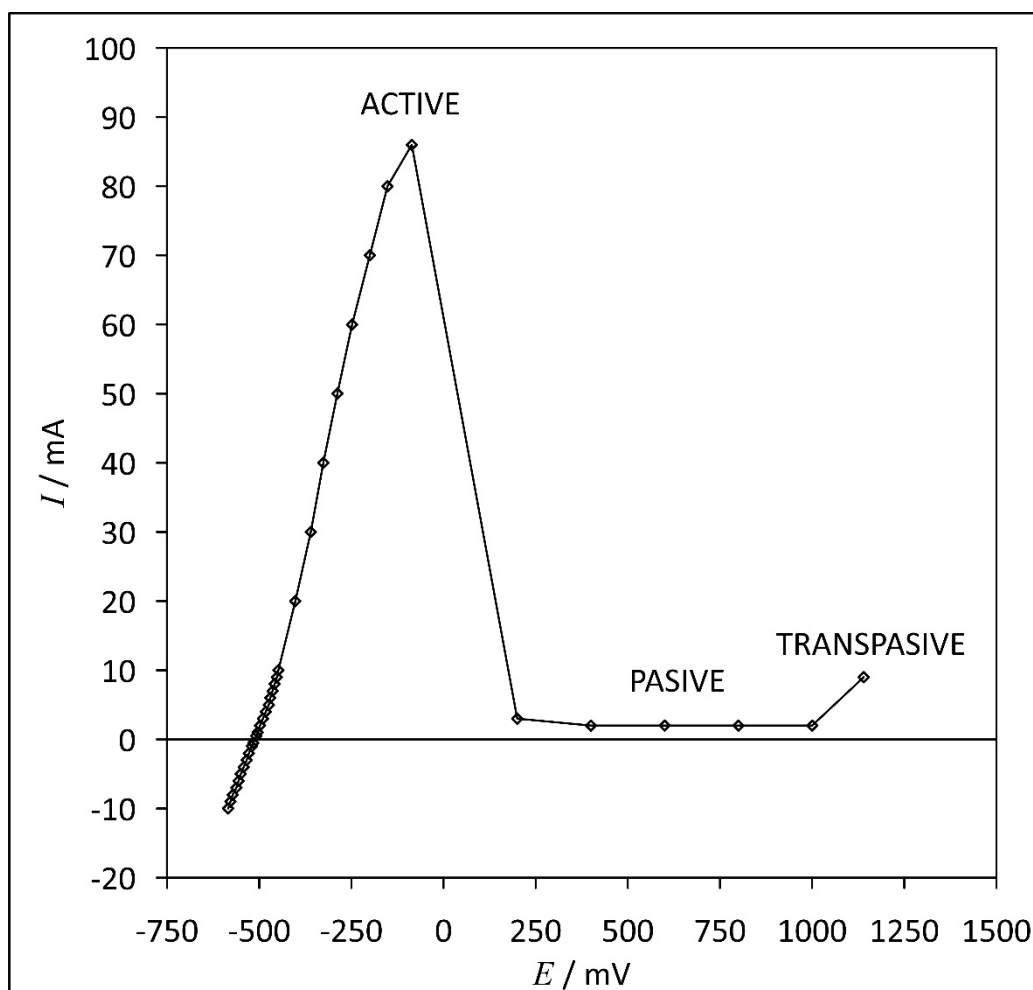
Figure 2.1: Current regarding potential graph.

During corrosion, several cathodic and anodic reactions take place at the same time. Mixed potential is commonly referred to as corrosion potential (E_{kor}). This is the potential at which the total rate of all anode reactions is equal to the total rate of the cathode reactions. The current density at the corrosion potential is called the corrosion current density and is a measure of the corrosion rate.

The corrosion current density is not measured directly, as the current flows between numerous microscopic cathode and anode sites on the surface. A "potentiostat" conected to a reference saturated calomel electrode is used for measurement. With the potentiostat, we cause a current to flow between the working and the counter-electrode, thus achieving a change in the potential of the working electrode towards the saturated calomel electrode. The polarization curves are shown using a current-petential graph, ploting the current on a logarithmic scale - Figure 2.2.
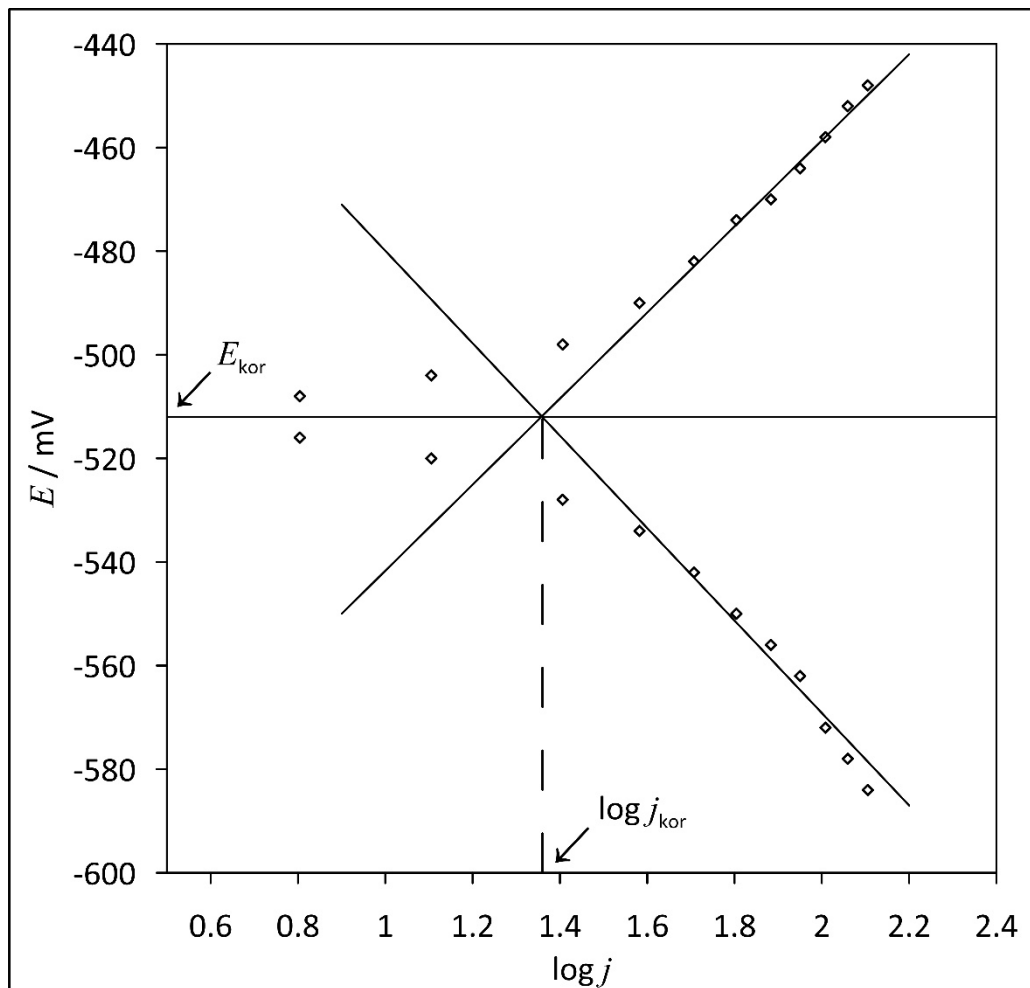
Figure 2.2: Polarization curve.

During the experiment, the sample is cathoded first, namely to E_{kor}, where the current density is zero. Then gradually change the potential on the sample to the anode range. According to the theory, we would get a linear dependence in the cathode and anode ranges. Test curves deviate slightly from linearity, but they have linear ranges called Tafel zones. Extrapolating these areas to E_{kor} yields j_{kor} and using this value we can calculate the corrosion rate according to Faraday's law:

$$r = \frac{M}{z} \frac{j_{kor}}{F} \tag{2.4}$$

where: M molar mass, z number of electrons, j current density and F Faraday charge ($\frac{M}{z} = 31.2$ g·mol^{-1}).

The current density is calculated as:

$$j = \frac{I}{A} \tag{2.5}$$

where: I current and A surface of the sample exposed to the corrosive medium.

a) Clasic method

Accessories and chemicals

− 1 L Erlenmeyer flask,
− condenser,
− 1 mol·L^{-1} H$_2$SO$_4$,
− diluted HNO$_3$ (1:10),
− acetone,
− glass sample holder.

Experimental Procedure

Immerse the Erlenmeyer flask containing 900 mL of 1 mol·L^{-1} H$_2$SO$_4$ in the thermostat. Measure the metal sample in order to determine its surface area. Hang the cleaned sample on a glass holder attached to the condenser and immerse in the H$_2$SO$_4$ for 40 minutes. After 40 minutes, the sample is chemically cleaned by immersing it in diluted solution of HNO$_3$ for a few seconds, and then for a couple of seconds in acetone. Dry and weigh the sample. Repeat the procedure three times.

Calculation And Results

− create a table with the time, mass of the sample before and after the experiment and mass loss,
− plot graph mass loss regarding time,

– calculate the corrosion rate in $g \cdot m^{-2} \cdot d^{-1}$.

b) Electrochemical method

Accessories and chemicals

– grinding paper,
– 1 mol·L^{-1} H$_2$SO$_4$,
– polarization cell,
– reference calomel electrode,
– saturated solution of KCl,
– potentiometer,
– amperemeter,
– tweezers,
– acetone.

Experimental procedure

The polarizing cell is of a standard shape. The cell has a volume of 1 L and is equipped with five conical grinds and one ball grind for the installation of an electrolytic key. Two openings are intended for counter-electrodes. One opening allows pirging with gases, and the middle, larger opening is intended for the sample holder (working electrode). One opening is designed for the thermometer. The holder for the working electrode is made of PTFE (Teflon). The reference electrode is a saturated calomel electrode. It is placed outside the polarization cell in a beaker with a saturated solution of KCl. A glass electrolytic key is filled with 1 mol·L^{-1} H$_2$SO$_4$.

With the potentiostat, change the potential of the working electrode against the saturated calomel electrode. With each change, read the appropriate current.

Calculation and results

– create a table with the current, potential, and current density,
– plot graph current regarding potential,
– plot polarization diagram, which shows the dependence of the current density on the potential,

– read the corrosion current density from the polarization diagram, j_{kor},
– calculate the corrosion rate in $g \cdot m^{-2} \cdot d^{-1}$.

c) Contact corrosion

Accessories and chemicals

– wires from Zn, Al, Fe, Cu and Pt,
– petri dish,
– $0.1 \ mol \cdot L^{-1}$ HCl,
– microscope.

Experimental procedure

The contact of two different metals - precious and non-precious - in $0.1 \ mol \cdot L^{-1}$ HCl causes contact corrosion and thus cathodic development of gas bubbles.

First, immerse each selected metal pair in the solution and observe for approximately one minute. Then, place the wires on top of each other and observe again. We use the following combinations of metals:

Zn - Pt	Al - Pt
Zn - Cu	Al - Cu
Zn - Fe	Al - Fe

Calculation and results

– create a table with descriptions of the changes on the metals and the nature of the reaction (qualitatively),
– write the reactions that take place at the cathode and anode for each pair of metals,
– calculate the standard potential of the pair, E^0:

$$E^0 = E_K^0 - E_A^0 \tag{2.6}$$

where: E_K^0 the standard potential of the cathode, and E_A^0 standard potential of anode,

- calculate the change in the standard Gibbs energy, ΔG^0, fro each pair,

$$\Delta G^0 = -z\,F\,E^0 \tag{2.7}$$

where: z the number of electrons exchanged during the reaction and F Faraday charge.

d) Eutectic mixture

Accessories and chemicals

- menthol crystals (melting point at 44 °C),
- phenol crystals (melting point at 41 °C),
- watch glass,
- microscope.

Experimental procedure

Two-component alloy systems can be single-phase (solid solutions) or two-phase (if the solubility limit is exceeded). For the study of two-component systems, phase diagrams are best suited, showing the relationship between the composition of the material, the composition of the phase and the temperature at equilibrium conditions and constant pressure.

The concept of eutectics is encountered in a diagram of two metals that are completely insoluble with each other. Examples of eutectic are mostly carried out at high temperatures. The use of the NaCl system - ice is suitable for testing at room temperature. A a simple demonstration, we will use the menthol-phenol system.

Put phenol and menthol crystals on a watch glass and give them together. Observe the process under a microscope. At the moment of contact, the crystals liquefy. We observe the transition from a solid to a liquid state. Using experimentally determined cooling curves of various mixtures of the system under consideration, the eutectic composition at 50 mol % menthol and the eutectic temperature at 30 °C were determined.

Calculation and results

- based on the given data, sketch an approximate phase diagram and explain the phenomenon.

Inhibitory Effect on Corrosion Resistance of Materials

Purpose of the exercise

Stainless steels are used in various fields both in experimental laboratory work and in industry, exposing them to corrosive media. Corrosion occurs not only in the production process, but also during cleaning, descaling and etching of process equipment. The most suitable, effective and economically acceptable method of inhibition or prevention of corrosion processes is the addition of inhibitors to corrosion media. Inhibitors are chemical substances that are physically or chemically absorbed onto the surface of a metal sample and thereby prevent reactions in the corrosion process (anode, cathode, or both). Inorganic and organic inhibitors are known. The choice of inhibitor is related to the purpose of use. Some inhibitors are toxic (chromates and dichromates), so alternative inhibitors (nitrites, nitrates, phosphates, silicates or molybdates) are increasingly used.

Theoretical background

Corrosion rate, r, according to the classical method is calculated as the loss of mass of the material on a given surface:

$$r = \frac{\Delta m}{A\,t} \tag{3.1}$$

where: t exposure time, A surface area of the sample and Δm mass, calculated as:

$$\Delta m = m_0 - m \tag{3.2}$$

where: m_0 initial mass of the sample and m mass of the sample after exposure to the corrosive medium.

Efficiency of the selected inhibitor, IE, is calculated:

$$IE = \frac{r - r_{inh}}{r}\ 100 \tag{3.3}$$

where: r corrosion rate without added inhibitor and r_{inh} corrosion rate with added inhibitor.

Accessories and chemicals

– metal samples,
– grinding paper (220, 400, 600, 1000 and 2000),

- beakers,
- desiccator,
- 0,1 mol·L^{-1} H$_2$SO$_4$,,
- acetone,
- NaNO$_2$,
- Na$_3$PO$_4$,
- borax (Na$_2$B$_4$O$_7$),
- Triton X-100.

Experimental procedure

Metal samples are grinded under running water starting with the coarsest grind paper and ending with fine grinding (220, 400, 600, 1000 and 2000). After grinding, measure the samples in order to calculate their surface area. Then they are washed with distilled water, immersed in acetone for a couple of seconds, dried and placed in a desiccator for 5 minutes. Weigh the samples. Prepare 0.1 mol·L^{-1} H$_2$SO$_4$. Fill the beakers with 500 ml of prepared acid. Add an inhibitor to one of the beakers, add different amounts of a particular inhibitor to the others. The inhibitory effect will be tested with four different inhibitors: borax - Na$_2$B$_4$O$_7$ ((1, 2.5, 5, 8) g), Na$_3$PO$_4$ ((0.25, 1, 2.5, 5) g), NaNO$_2$ ((0.25, 0.5, 1, 2) g) and Triton X-100 ((0.5, 1, 1.5 in 2) mL 1000 x diluted solution of Triton X-100)). Dip one prepared sample into each beaker. Turn on the air supply. After 2 hours, brush the samples under running water, wash with distilled water, immerse in acetone for a couple of seconds, dry and place in a desiccator for 5 minutes. Weigh the samples.

Calculation and results

- create a table with the mass of the sample before and after the experiment, mass loss, corrosion rate without and with added inhibitor and inhibitor efficiency,
- plot graph corrosion rates regarding mass/volume of the inhibitor,
- plot graph efficiency of inhibitor regarding mass/volume of the inhibitor.

4. **EXERCISE**

Fluidization

Purpose of the exercise

Fluidization is a process in which solids behave like fluids. When a liquid or gas travels through a layer of solid particles:

- at a very low fluid flow, the solid particles do not move,
- as the flow rate increases, the upward pulling force per individual particle also increases,
- if the flow rate increases further, at a certain flow, the particles begin to move and become suspended in the fluid.

The suspension of solid particles in a fluid is called a fluidized layer and the process is called fluidization. Fluidization is applied in catalyzed and non-catalyzed reactions, in the process of drying solid particles, separation of particles of different sizes, heat treatment and transport of solid particles.

Theoretical background

Two forces act on the particles in the bed. The upward force is expressed as:

$$F_{\uparrow} = \Delta p \, A \tag{4.1}$$

where: Δp pressure change and A surface – cross-section of the bed. The downward force is expressed as:

$$F_{\downarrow} = l \, A \, (1 - \varepsilon) \left(\rho_s - \rho_f \right) g \tag{4.2}$$

where: l height of the bed, ε void coefficient (usually 0.4), ρ_s particle density in the bed (2500 kg·m^{-3}), ρ_f density of the fluid and g gravitational acceleration. The pressure drop or pressure change required for fluidization occurs when the upward force is equal to the downward force. If we combine equations 4.1 and 4.2, we can calculate the change in pressure that is necessary for fluidization to occur:

$$\Delta p_f = l \, (1 - \varepsilon) \left(\rho_s - \rho_f \right) g \tag{4.3}$$

The average surface velocity through the bed in the reactor is calculated:

$$v = \frac{q_f}{A} \tag{4.4}$$

where: q_f fluid flow.

The Carman-Kozeny equation for calculating the change in pressure is expressed as:

$$\Delta p = \frac{180 \, l \, \mu \, (1-\epsilon)^2 \, v}{\phi^2 \, d_s^2 \, \epsilon^3}$$
(4.5)

where: μ dynamic viscosity of the fluid, ϕ sphericity (for round particles 1) and d_s diameter of particles in the bed.

Accessories and chemicals

– glass granulate with diameter (0.625 in 0.25) mm,
– deionized water,
– compressed air.

Experimental procedure

Before the experiment, check that the apparatus is connected to the compressed air supply (the pressure should be set between 2 – 8 bar) and that the base of the apparatus is filled with deionized water (the water level should be about 5 cm below the plate on which the reactors are located). If the values for water and air flow and pressure change on the display are not 0, then press the Tare button. In front of each reactor there is a regulator – a valve for regulating the flow of fluid through the reactor. Regulator – the valve is opened clockwise and closed counterclockwise. It has a built-in barrier, it needs to be raised so that it can be turned.

The apparatus consists of three reactors - towers. One is designed for water handling and is filled with Ballotini glass granules with particle size of 0.625 mm. Two of them are designed for air operation and are filled with Ballotini glass granules with a particle size of 0.625 mm (Air 1) and 0.25 mm (Air 2). Experiments will be carried out in all three reactors.

Turn on the pump for pumping deionized water. Increase the water flow by 0.05 L·min^{-1} by slowly turning the regulator (H$_2$O) clockwise. When the equilibrium state is established at individual flow, write down the flow rate value, the pressure change and the height of the bed. Observe how the glass granulate behaves in the reactor.

Open the valve for the supply of compressed air. Increase the air flow by 0.5 L·min^{-1} by slowly turning the regulator (Air 1) clockwise. When the equilibrium state is established at individual flow, write down the flow rate value, the pressure change and the height of the bed. Observe how the glass granulate behaves in the reactor. Repeat the procedure for the second reactor in which we have a different size of glass granulate (Air 2).

Calculation and results

– create a table with the temperature at which you performed the experiment, water density, density of the air, dynamic viscosity of water and dynamic viscosity of air,
– for each individual reactor, calculate the pressure change when fluidization occurs,
– create a table with water or air flow, pressure change, height of the bed, calculated values of average surface velocity and calculated values of pressure change,
– plot graph pressure change regarding fluid flow (water/air),
– plot graph height of the bed regarding fluid flow (water/air).

Suggested Additional Study Literature

1.   Levenspiel Octave, Chemical Reaction Engineering, Third Edition, Wiley, 1998.
2.   Instruction manual for CEU Catalytic Reactors, Armfield.
3.   Instruction manual for CEL-MKII Fixed and Fluidised Bed Apparatus, Armfield.

Chemical Reaction Engineering II: Manual for Performing Laboratory Exercises

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Manual for performing laboratory exercises in the course Chemical Reaction Engineering II represents a teaching aid for students to be able to approach experimental work in the laboratory.