

Electrodiffusion characterization of non-Newtonian flow through packed beds*

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The limiting current technique, involving the cathodic controlled reduction of ferricyanide ions, has been used in order to characterize the axial dispersion and the solid-liquid mass transfer for a non-Newtonian shear thinning power-law fluid flowing through fixed beds of spherical and parallelepipedal particles. For each of the two phenomena, results corresponding to Newtonian and non-Newtonian power-law flow at low Reynolds numbers can be described by the same dimensionless equation for beds packed with particles of the same shape.

1. Introduction

The knowledge of the behaviour of non-Newtonian flow through porous media has applications in important areas such as petroleum reservoir engineering, oil recovery from water flooding using non-Newtonian polymers solutions as displacing fluids, flow through ion exchange beds, ground water hydrology, polymer processing etc.

Whereas many experimental and theoretical studies are concerned with pressure drop determination, only a few deal with axial dispersion [1-4] and liquid-solid mass transfer [5, 6] during flow of non-Newtonian fluids through porous media.

In order to obtain additional data, the limiting current technique has been used for studying these two phenomena in the case of a purely viscous shear thinning power-law electrolyte flowing through beds tightly packed with spheres of different diameters and with anisotropic square based parallelepipedal particles, respectively.

2. Characteristics of the non-Newtonian solution

The non-Newtonian electrolyte A was an aqueous solution of carboxymethyl cellulose sodium salt 6 kg m^{-3} (BDH high viscosity), potassium ferricyanide 1 mol m^{-3} , potassium ferrocyanide 10 mol m^{-3} , sodium carbonate 10^2 mol m^{-3} , sodium hydrogenocarbonate 10^2 mol m^{-3} . Its density was $\rho = 1022 \text{ kg m}^{-3}$ at 25°C .

The behaviour of this polymer solution can be described in terms of the power-law model. The consistency index, K , and the behaviour index, n , were determined from shear stress, τ , against shear rate, $\dot{\gamma}$, data obtained in a rotational rheometer using a double gap concentric cylinder. The rheological equation, at 25°C may be written

$$\tau = 0.175 \dot{\gamma}^{0.72} \quad \text{for } 20 \text{ s}^{-1} < \dot{\gamma} < 1200 \text{ s}^{-1} \quad (1)$$

with a mean relative quadratic error lower than 5%. The value $\dot{\gamma} = 1200 \text{ s}^{-1}$ corresponds to the largest estimated value of shear rate reached in mass transfer experiments.

The diffusion coefficient, D , of the ferricyanide ions was evaluated with a rotating platinum disk electrode of radius $R = 10^{-3} \text{ m}$. The limiting current obtained from current-potential curves corresponding to ferricyanide ion reduction at the disc was correlated to the rotation speed Ω by the equation

$$I_L = 4.810 \cdot 10^{-7} \Omega^{0.57}$$

with

$$46 < \Omega < 524 \text{ s}^{-1} \text{ (SI units)} \quad (2)$$

The equation giving the average molar flux at the disc $J = I_L / F\pi R^2$ was derived analytically by Greif and Paterson [7]:

$$J = \frac{N(n)}{0.893} C_0 D^{2/3} (K/\rho)^{-1/3(1+n)} R^{(1-n)/3(1+n)} \Omega^{1/(n+1)} \quad (3)$$

where C_0 is the concentration of ferricyanide ions in the solution, F is the Faraday number, and

$$N(n) = \left[12a \left(\frac{1+n}{7+5n} \right)^2 \right]^{1/3} \quad (4)$$

The values of coefficients were tabulated by Mitschka and Ulbrecht [8] for n varying from 0.2 to 1.5. Equations 2, 3 and 4 yield $n = 0.75$ close to the value $n = 0.72$ determined with the rheometer and $D = 5.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

3. Axial dispersion

3.1. Experimental procedure and calculation of the axial dispersion coefficient D_{ax}

The apparatus is shown in Fig. 1. The liquid

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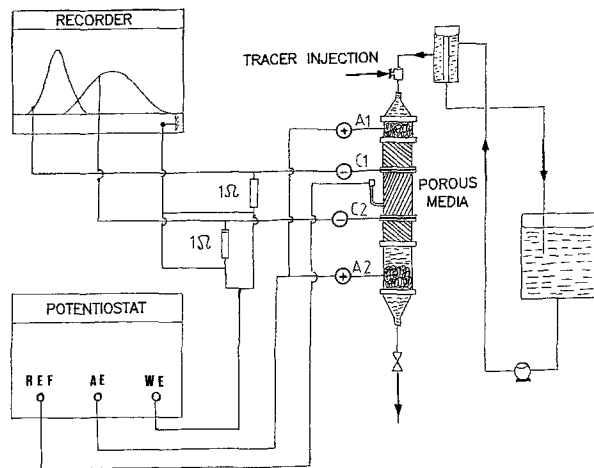


Fig. 1. Schematic diagram of experimental method used for D_{ax} determination.

introduced at the top of the column flowed from a constant level tank through the packed bed divided into three parts: an entrance and calming section IC_1 , a test section C_1C_2 and an exit section C_2O . The test section C_1C_2 , 0.15 m high, was located between two identical nickel grids C_1 and C_2 . The flow behaviour through the test section was studied by means of the experimental determination of the residence time distribution (r.t.d.) of the liquid in this section. The r.t.d. was obtained by an electrochemical method identical to that currently used in the measurement of solid to liquid mass transfer coefficients [9].

Both nickel grids C_1 and C_2 were working as cathodes where the electrochemical reduction of the ferricyanide ions occurs under limiting diffusion conditions. The two anodes, A_1 and A_2 , of large surface area (knits of nickel wire) were located respectively at the entrance and the bottom of the column.

The experimental method consisted in injecting a small volume of initial electrolyte saturated with potassium ferricyanide before the column entrance and in registering the current as a function of time simultaneously at both cathods C_1 and C_2 . In given hydrodynamic conditions, the mean mass transfer coefficient, k , between the flowing liquid and each grid is constant, therefore the limiting diffusion current $I_L(t)$ at a grid is directly proportional to the ferricyanide ion concentration, $c(t)$, in the liquid flowing through the corresponding grid. If I_{L0} is the limiting diffusion current before injection, the value of $(I_L(t) - I_{L0})$ is directly proportional to the tracer concentration.

The normalized signals $y_1(t)$ and $y_2(t)$, respectively, on detectors C_1 and C_2 are calculated by:

$$y_1(t) = \frac{I_{L1}(t) - I_{L10}}{\int_0^{2T} (I_{L1}(t) - I_{L10}) dt}$$

and

$$y_2(t) = \frac{I_{L2}(t) - I_{L20}}{\int_0^{2T} (I_{L2}(t) - I_{L20}) dt}$$

where $2T$ is the time required to allow the response signal $y_2(t)$ to vanish: $I_{L2}(2T) = I_{L20}$.

The analysis of the experimental responses $y_1(t)$ and

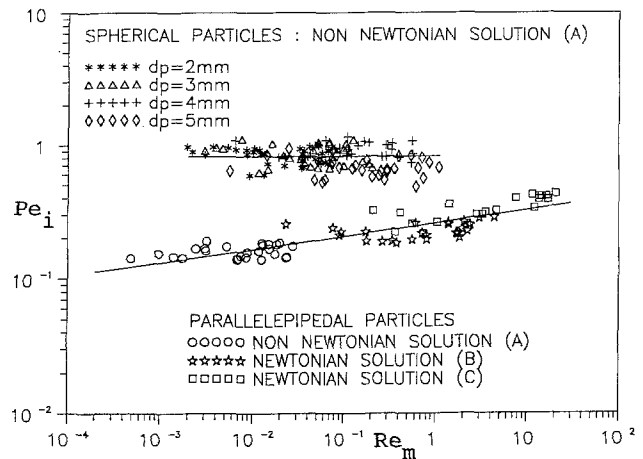


Fig. 2. Pe_i against Re_m for spherical and parallelepipedal particles.

$y_2(t)$ on the two detectors at a tracer injection was made by the curve fitting method in the time domain [10]. This method is based on the comparison of the experimental response $y_2(t)$ with the response calculated from the experimental response $y_1(t)$ on C_1 , by using the transfer function of the dispersed plug flow model. The two parameters derived from this identification are the mean residence time and the axial dispersion coefficient D_{ax} .

Additional information on the experimental and the calculation methods can be found in [11, 12] concerned with Newtonian fluid flow through packed beds of parallelepipedal particles.

3.2. Experimental results and correlating equations

In order to correlate the experimental results by dimensionless equations, the following dimensionless numbers were used: interstitial Peclet number: $Pe_i = U_o d_p / \varepsilon D_{ax}$, modified Reynolds number:

$$Re_m = \left(\frac{\rho U_o^{2n-2} d_p^n}{K} \right) \left[\frac{\varepsilon^{2n-2}}{((3n+1)/4n)^n (1-\varepsilon)^n 12^{n-1}} \right]$$

where U_o is the superficial velocity and ε the bed void fraction.

3.2.1. Spherical particles. Tightly packed beds of spheres of diameter 2×10^{-3} m, 3×10^{-3} m, 4×10^{-3} m, 5×10^{-3} m and bed void fraction $\varepsilon = 0.36$ were studied. The interstitial velocity U_o/ε was varied from 10^{-4} m s $^{-1}$ to 2×10^{-2} m s $^{-1}$. All our experiments (136 experimental points) are represented by a single equation (Fig. 2):

$$Pe_i = 0.82 \pm 0.15 \quad \text{for} \quad 2 \times 10^{-3} < Re_m < 1.1 \quad (5)$$

This value is nearly identical to that obtained for Newtonian flow [13, 14].

3.2.2. Parallelepipedal particles. Axial dispersion in liquid flow through a bed tightly packed with square based parallelepipedal particles (thickness $h = 1.045 \times 10^{-3}$ m, side $s = 5 \times 10^{-3}$ m) was studied. The bed void fraction was 0.35.

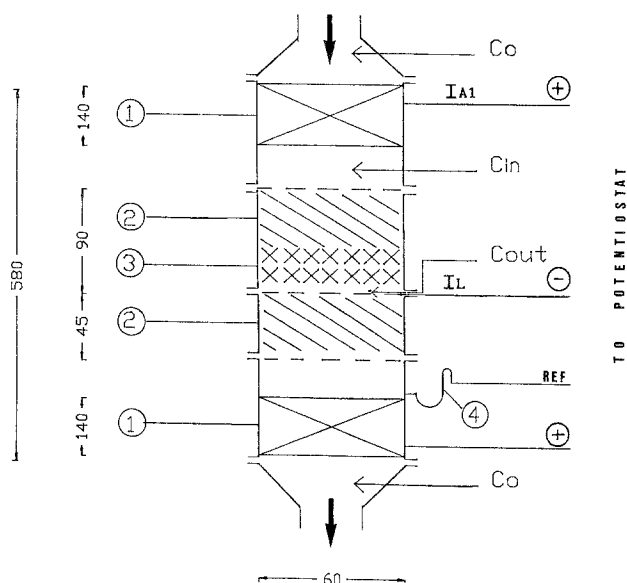


Fig. 3. Test column used in mass transfer experiments: (1) anodes, (2) fixed beds of inert particles, (3) cathode: fixed bed of active particles supported by a nickel grid, (4) reference electrode (all dimensions in mm).

Two solutions were used: the previous non-Newtonian electrolyte A and a Newtonian one B: $K_3Fe(CN)_6$ 1 mol m^{-3} , $K_4Fe(CN)_6$ 10 mol m^{-3} , $NaOH$ 10^2 mol m^{-3} , Polyethylene glycol 6000 (200 kg m^{-3}), the dynamic viscosity of which was $\mu = 9.7 \times 10^{-3} \text{ Pa s}$. The results obtained in the same experimental conditions for the Newtonian solution C of lower viscosity $\mu = 1.07 \times 10^{-3} \text{ Pa s}$, previously published [11, 12], are also shown on Fig. 2.

It may be observed that all experimental results corresponding to the Newtonian and non-Newtonian solutions are well correlated by a single equation (Fig. 2):

$$Pe_i = 0.26 Re_m^{0.10} \quad (6)$$

with a mean quadratic relative error $q = 0.16$.

The equivalent diameter of the particle used in the Peclet and Reynolds numbers is defined by $d_p = 6/a_v$ where a_v is the specific surface area of the particles.

4. Mass transfer

4.1. Experimental method and calculation of the mean mass transfer coefficient

The mean liquid-solid mass transfer coefficient, k , between the non-Newtonian flowing electrolyte and the packed bed was obtained electrochemically using the cathodic reduction of ferricyanide ions. The method was previously described in [11] and [15] corresponding to Newtonian fluid flow through fixed beds of parallelepipedal particles. The test column used for the measurements is shown in Fig. 3.

The packed bed for the mass transfer study was a tightly packed bed of nickel particles supported by a

nickel grid cathode (current feeder). It was located between two identical fixed beds of inert particles. The experiments were performed with different active bed heights. The anodes were two identical knits of nickel wire of large surface area located, respectively, upstream and downstream from the cathode in order to reduce the overall solution potential drop in the cathodic bed [16].

For each liquid flow rate measured by an electromagnetic flow-meter, the overall limiting current at the cathode, I_L , was obtained from the current potential curve. I_L is the sum of two terms: $(I_L)_c$ corresponding to the cathodic bed and $(I_L)_G$ corresponding to the grid. Thus the conversion through the active bed X is

$$X = 1 - \frac{C_{out}}{C_{in}} = \frac{I_L - (I_L)_G}{FQ_v C_o + I_{A1}} \quad (7)$$

Where C_{in} , C_{out} and C_o are the ferricyanide concentrations, respectively, at the bed entrance, the bed exit and in the tank, Q_v is the volumetric electrolyte flow rate, I_{A1} the current intensity measured at the top anode. The values of $(I_L)_G$ were obtained by using inert particles identical to the nickel ones.

The constant k was calculated from the differential equation of the dispersed plug flow model. Its solution was obtained by considering that the active bed is open to dispersion at its two extremities [17, 18, 15].

4.2. Results

The experimental results were correlated by a dimensionless equation of the type

$$\varepsilon J_d = A Re_m^z \quad (8)$$

with $J_d = Sh Re_m^{-1} Sc_m^{-1/3}$ (Chilton Colburn mass transfer factor), $Sh = k d_p/D$ (Sherwood number), and the modified Schmidt number given by

$$Sc_m = \frac{K}{\rho D} \left[\frac{3n+1}{4n} \right]^n \left(\frac{8U_o}{\varepsilon} \right)^{n-1} \left[\frac{3(1-\varepsilon)}{2d_p \varepsilon} \right]^{n-1}$$

4.2.1. Spherical particles. Active fixed beds of nickel spheres of diameter $2 \times 10^{-3} \text{ m}$, $3 \times 10^{-3} \text{ m}$, $4 \times 10^{-3} \text{ m}$, $5 \times 10^{-3} \text{ m}$ were studied using different heights, H , varying from 10^{-2} m to $4 \times 10^{-2} \text{ m}$. From all the experiments (18 independent series corresponding to 401 points) a single correlating equation was determined

$$\varepsilon J_d = 1.02 Re_m^{-0.62} \quad \text{for } 0.0032 < Re_m < 5.7 \quad (9)$$

with a mean quadratic error $q = 0.147$ (Fig. 4).

The line 1 on Fig. 4 corresponds to the correlation obtained by Kumar and Upadhyay [5] for a power-law fluid ($n = 0.85$) by using the dissolution method ($A = 0.803$, $\alpha = -0.72$, calculated with $\varepsilon = 0.36$, with an average deviation of $\pm 19\%$ for $0.06 < Re_m < 15.6$). The scatter with our results may be explained by the two following reasons: (i) that Kumar and Upadhyay did not take axial dispersion into account and (ii) that the surface area of the

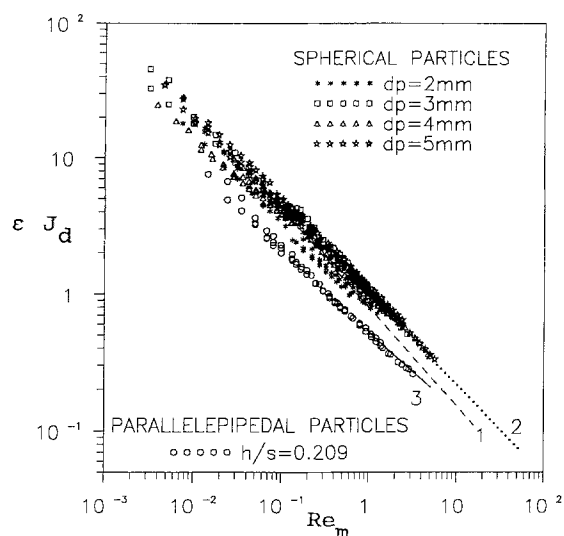


Fig. 4. εJ_d against Re_m . Spheres particles, d_p : *, \square , \triangle , \star , \diamond our experimental data for non-Newtonian solution A; (---) equation of Kumar *et al.* [5] for non-Newtonian fluids; (····) equation of Coeuret [18] for Newtonian fluids. Parallelepipedal particles: (O) our experimental data for solution A, (—) equation of Comiti *et al.* [15] for Newtonian fluids.

particles using a dissolution method varies slightly as a function of time.

Line 2 on Fig. 4 ($A = 1.0$ $\alpha = -2/3$ for $0.07 < Re_m < 51$) is representative of the results obtained for Newtonian flow by Coeuret [19], who took axial dispersion into account and used the electrochemical method. A good agreement with our results for non Newtonian fluid flow is observed. This equation represents our experimental results for $0.07 < Re_m < 5.7$ with a mean relative quadratic error $q' = 0.15$, nearly identical to the value of q .

4.2.2. Parallelepipedal particles. Liquid-solid mass transfer was studied for beds tightly packed with square based nickel parallelepipedal particles (thickness $h = 1.075 \times 10^{-3}$ m, side $s = 5.145 \times 10^{-3}$ m, bed void fraction $\varepsilon = 0.35$) for different heights ($H = 10^{-2}$ m, 1.5×10^{-2} m and 2×10^{-2} m). All the results are correlated by:

$$\varepsilon J_d = 0.50 Re_m^{-0.62} \quad \text{for } 0.008 < Re_m < 3.2 \quad (10)$$

with a mean quadratic relative error $q = 0.051$.

It may be observed on Fig. 4 that there is good agreement with results previously obtained in the same experimental conditions for a Newtonian solution (line 3) [11, 15].

5. Conclusion

The electrochemical method was successfully used to characterize axial dispersion and mass transfer for non-Newtonian power-law flow through packed beds at low Reynolds numbers.

For each of the two phenomena, results corresponding to Newtonian and non-Newtonian purely viscous liquid flows studied in this work can be represented by the same dimensionless equation for beds packed with particles of the same shape.

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