

Axial dispersion in flow porous electrodes

R. E. SIODA

Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, ul. Kasprzaka 44, Poland

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The coefficient of axial dispersion D_L in a porous electrode, composed of rolled 80-mesh platinum screen, was determined using the process of the flow electrolysis of 2.0×10^{-3} M $K_3Fe(CN)_6$ in 1 M KCl in water. The results were analysed in the light of an earlier model for flow electrodes.

List of symbols

a	Electrode cross-sectional area (cm^2)
b	Empirical constant
c_0	Initial concentration of substrate ($mol\ ml^{-1}$)
D_L	Axial dispersion coefficient ($cm^2\ s^{-1}$)
D^*	Effective dispersion coefficient ($cm^2\ s^{-1}$)
F	Faraday constant ($C\ mol^{-1}$)
I_1	Limiting current (A)
L	Electrode height (cm)
R	Limiting degree of conversion of substance
v	Volume flow rate ($ml\ s^{-1}$)
α	Empirical constant
ϵ	Electrode porosity

1. Introduction

The theory of dispersion in tubular chemical reactors was developed by Danckwerts [1] whose results have been applied by the present author [2, 3], and recently also by Coeuret [4] to electrolysis on porous electrodes subjected to solution flow (flow porous electrodes). The theory has been experimentally confirmed for graphite porous electrodes [3], which has shown that the decrease of the slope of $\log\text{-}\log [1/(1-R)]$ versus $\log v$ lines can be explained by dispersion.

In this paper another method for the analysis of experimental data for flow porous electrodes is shown which also permits evaluation of the dispersion coefficient. This method is illustrated by experimental results obtained for a flow porous electrode composed of an 80-mesh platinum screen.

2. Results and discussion

The results were obtained for a flow porous electrode composed of a rolled 80-mesh platinum screen using the experimental technique previously described [5, 6]. The measured dependence of the limiting current and the solution flow rate for the process of reduction of a 2.0×10^{-3} M solution of $K_3Fe(CN)_6$ in 1 M KCl in water is shown using logarithmic co-ordinates in Fig. 1. The experimental points in the range of higher flow rates ($0.18 < v/ml\ s^{-1} < 0.93$) were analysed previously, using the model of flow porous electrodes suitable for conditions when dispersion has a negligible role. The points in this range are described by the following equation containing empirical constants determined by the least squares method:

$$I_1 = nFc_0v[1 - \exp(-0.208v^{-0.63})]. \quad (1)$$

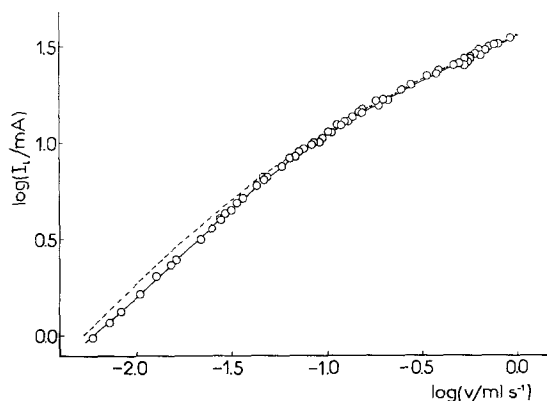


Fig. 1. The experimental dependence of the limiting current of the reduction of $K_3Fe(CN)_6$ on solution flow rate. The curves correspond to semi-empirical Equations 1 (dotted curve) and 6 (solid curve).

The curve drawn according to Equation 1 is shown in Fig. 1 with a dotted line. The curve satisfactorily describes the experimental points in the range of the higher flow rates, but is too high for small flow rates. In the latter region, the more general model of flow porous electrodes, including dispersion, should be applied. According to this model, the limiting current is equal to:

$$I_1 = nFc_0v[1 - (1 + b^2D^*a^{(3-2\alpha)}v^{(2\alpha-3)}L) \times \exp(-bLa^{(1-\alpha)}v^{(\alpha-1)})]. \quad (2)$$

At higher flow rates the term, $v^{(2\alpha-3)}$ tends to zero (α being a fraction of unity), and Equation 2 reduces to:

$$I_1 = nFc_0v[1 - \exp(-bLa^{(1-\alpha)}v^{(\alpha-1)})]. \quad (3)$$

Equation 1 has a form consistent with Equation 3.

For the experimental checking of Equation 2, and determination of the effective coefficient of dispersion D^* , it is convenient to transform Equation 2 to the following form:

$$\begin{aligned} \exp[\ln(1-R) + bLa^{(1-\alpha)}v^{(\alpha-1)}] - 1 \\ = b^2D^*La^{(3-2\alpha)}v^{(2\alpha-3)} \end{aligned} \quad (4)$$

where R denotes the limiting degree of conversion [6]:

$$R = \frac{I_1}{nFc_0v} \quad (5)$$

The left-hand side of Equation 4 can be calculated from the magnitude of the limiting current by Equation 5, and using constants b and α determined by means of Equation 3 for the range of higher flow rates. On the right-hand side of Equation 4 is the unknown effective coefficient of dispersion D^* . A logarithmic plot of the dependence of the left-hand side of Equation 4 on $v^{(2\alpha-3)}$ should give a straight line of slope equal to unity. From the intercept of the line D^* is calculated. Such a plot for the experimental points of Fig. 1 in the low range of flow rates ($0.0058 < v \text{ ml s}^{-1} < 0.037$) is shown in Fig. 2. In the calculations the values of the constants b and α determined earlier were used: $\alpha = 0.37$ and $b = 0.86$ [2]. The points in Fig. 2 form a straight line, which confirms the validity of Equations 4 and 2. The parameters of the line, determined by the least squares method, are as follows: slope 0.964, intercept -3.55 , standard deviations

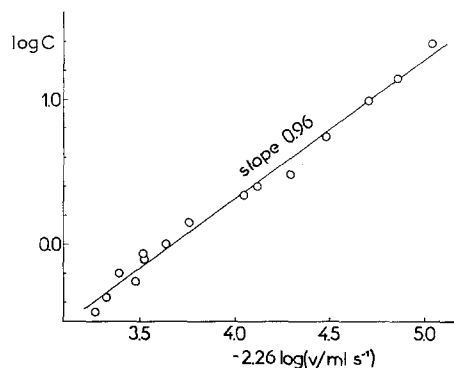


Fig. 2. The dependence of the logarithm of the left-hand side of Equation 4, denoted as C , on logarithm of the solution flow rate multiplied by -2.26 .

respectively 2.8% and 3.1%, square of the coefficient of correlation 0.990, and 95% confidence limits of the slope 0.90 to 1.02, and of the intercept -3.78 to -3.31 . The value of the slope differs only slightly from the expected value unity. The difference can probably be attributed to small variations of the constants b and α , and/or of the effective dispersion coefficient D^* in the investigated range of the flow rates. From the intercept of the line in Fig. 2 the effective dispersion coefficient is calculated as $5.9 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$. In the calculation the following values of the geometric parameters of the electrode have been used: $a = 0.43 \text{ cm}^2$, and $L = 0.41 \text{ cm}$. The axial dispersion coefficient $D_L = D^*/\epsilon$ is equal to $7.4 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ and $\epsilon = 0.8$. The calculated value of D_L is much too high to be affected by molecular diffusion. Instead the determined D_L is due to mixing of the fluid in the porous medium, governed by statistical laws similar to the laws of diffusion [7, 8].

Substituting the determined numerical values into Equation 2 the following semi-empirical equation for the limiting current is obtained:

$$I_1 = nFc_0v[1 - (1 + 2.85 \times 10^{-4}v^{-2.18}) \times \exp(-0.208v^{-0.63})] \quad (6)$$

where v is expressed in ml s^{-1} . The curve corresponding to Equation 6 is shown in Fig. 1 with a solid line. The line represents the experimental points well in the whole investigated 150-fold range of the flow rates (from 0.0058 to 0.93 ml s^{-1}).

Substituting Equations 1 or 6 into Equation 5,

the corresponding dependences of the limiting degree of conversion on the solution flow rate are obtained. The respective plots are given in Fig. 3,

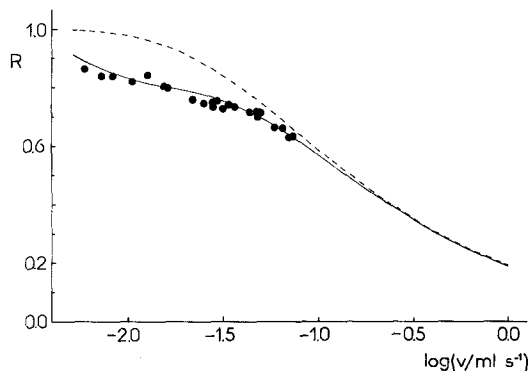


Fig. 3. The dependence of the limiting degree of conversion R on the logarithm of solution flow rate. The dotted curve is obtained from Equation 1, the solid curve from Equation 6, and the experimental points directly from Equation 5.

where the dotted line corresponds to Equation 1, and the solid line to Equation 6. For comparison the experimental points are given calculated according to Equation 5 directly from the pairs of

measured I_1 and v values. It is seen that only the solid line corresponding to Equation 6 represents the experimental points satisfactorily. In this low range of flow rates Equation 1 results in limiting degrees of conversion which are too high. It is interesting to see in Fig. 3 that both the experimental points and the curve calculated according to Equation 6 show a characteristic quasi-plateau in the lower range of flow rates.

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