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Mass Transfer Correlations for a Rotating Cylinder Electrode under Isothermal and Controlled Heat Transfer Condition

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Abstract

Mass transfer correlations for iron rotating cylinder electrode in chloride/sulphate solution, under isothermal and controlled heat transfer conditions, were derived. Limiting current density values for the oxygen reduction reaction from potentiostatic experiments at different bulk temperatures and various turbulent flow rates, under isothermal and heat transfer conditions, were used for such derivation. The corelations were analogous to that obtained by Eisenberg et al1 and other workers.

Introduction

The rotating cylinder electrode (RCE) has found a wide variety of applications in the investigation of corrosion processes under flow conditions, especially, when a naturally turbulent flow regime must be simulated 1-9. Such studies are of industrial importance and allow modelling and quantification of corrosion rates, when the process limited by the rate of mass transfer.

Chemical engineers have a tradition of evaluating transport properties for a particular system geometries and flow conditions by means γof dimensionless correlations. A well known mass transfer correlation for a RCE is that given by Eisenberg et al1 under isothermal conditions:

$$Sh = 0.079\, R_e^{0.7}\, Sc^{0.356} \qquad (1)$$

i.e.,

$$Sh = a\, R_e^{b}\, Sc^{c} \qquad (2)$$

Equation (2) is the general form of the mass transfer process where a , b and c are constants.The dimensionless quantities,Reynold'snumber(Re) ,Schmidt number (Sc) and sherwood number (Sh) are related to the physical properties of the fluid and system geometry by:

$$R_e = \frac{vd}{\gamma} \qquad (3.a)$$

$$Sc = \gamma / D \qquad (3.b)$$

$$Sh = \frac{K_c d}{D} \qquad (3.c)$$

For the limiting stage of the cathodic reduction reaction of oxygen at a metal surface, the limiting flux is:

$$N = K_c C_b \qquad (4)$$

And,

$$N = \frac{i_{lim}}{zF} \qquad (5)$$

Equating equations (4) and (5), therefore,

$$K_c = \frac{i_{lim}}{zFC_b} \qquad (6)$$

The mass transfer coefficient is expressed in terms of the Sherwood number (Sh), see Eq. (3.c)

Several correlations have been predicted by number of workers2-9, which are satisfactorily applied for electrochemical processes under turbulent flow conditions. These correlations are presented in Table (1) together with the working conditions. Table (1) shows that different values of empirical constants (a, b and c) have been obtained by the different authors.

Limiting current density data for the oxygen reduction reaction from potentiostatic experiments in 730 ppm chloride / 413 ppm sulphate solution, under isothermal and controlled mass transfer conditions, were used for this study. Electrolyte bulk temperature was controlled at 303, 313, and 323K (±0.1 K) and at various turbulent flow rates corresponding to 100, 200, 400 and 500 rpm using the RCE system. Corresponding data, under controlled heat transfer conditions were also used. The heat flux rate used was 12.063 kWm-2.

Experimental Work

The detailed designs of the apparatus used in this investigation and the experimental work were described elsewhere 10,11 .

The design of the RCE assembly, in addition to satisfying the fundamental requirements of the hydrodynamic theory, also required the provision of a heat transfer system with a means of measuring temperature at a various radial distances from the centre of the electrode shaft in order to determine the heat flux and to calculate the electrode interfacial temperature.

Results and Discussion

Isothermal Conditions.

Calculation of Mass Transfer Coefficient.

Using Eq. (6), the mass transfer coefficient, Kc , at the various flow rates and bulk temperatures was calculated using the experimental ilim values for the oxygen reduction reaction, z = 4 and the oxygen concentration, Cb11. The results are given in Table (2), which shows that Kc is both flow and temperature dependent.

Calculation of Sherwood Number

Using Eq. (3.c), the Sherwood number values at the various flow rates and bulk temperatures were calculated using the Kc values in Table (2), the diffusion coefficient, D11 and d = 68.3 mm. The calculation results are given in Table (3).

Table (3) shows that, at constant bulk temperature, the Sherwood number increases as the flow rate increases, due to the increase of Kc with flow rate. At constant flow rate, the change in Sherwood number with temperature is negligible. This is to be expected as the increase in Kc is counteracted by the increase in diffusion coefficient ,D .

Heat Transfer Conditions.

Calculation of Mass Transfer Coefficient.

In a similar way to that in Section (1.1), the Kc values, under heat transfer conditions, were calculated using the experimental ilim values for the oxygen reduction reaction, z = 4 and the oxygen concentration, Cb11 . The calculation results are given in Table (4) together with the interfacial temperatures (bracketed). Table (4) shows that Kc is both flow and temperature dependent.

Calculation of Sherwood Number.

The Sherwood number values, under heat transfer conditions, were calculated using Kc values in Table (4), the diffusion coefficient, D11 at the mean temperature 12-14, Tm* and d = 68.3 mm. The calculation results are given in Table (5) together with the interfacial temperatures (bracketed).

$$T_m* = \frac{T_b + T_i}{2}$$

Mass Transfer Correlations.

In the present work, it is intended to correlate the calculated Sherwood number in terms of Reynolds number , Re and Schmidt number, Sc, for isothermal and heat transfer conditions, to obtain a correlation for the studied system analogous to that obtained by Eisenberg et all and other workers.

Rearranging Eq. (2), and taking c=0.356, therefore,

Sh/Sc0.356 = a Reb (7)

Taking the Sherwood number values in Tables (3) and (5), the Kinematic viscosity, ν15, and the diffusion coefficient, D11, at bulk or mean temperature as appropriate, the values of Re, Sc, Sc0.356, Sh/Sc0.356 were calculated under both isothermal and heat transfer conditions. The calculation results are given in Tables (6.a-c) and (7.a-c) respectively.

The L.H.S. of Eq. (7) was plotted versus Re on Log - Log scale for both isothermal and heat transfer conditions as shown in Fig. (1).

Employing a computer programme (Grapher, IBM personal computer), the constants a and b were obtained. Therefore, Eq. (7) becomes:

for isothermal conditions:

$$Sh = 0.307\, Re^{0.624}\, Sc^{0.356} \qquad (8)$$

and for heat transfer conditions:

$$Sh = 0.159\, Re^{0.665}\, Sc^{0.356} \qquad (9)$$

Figure (1) shows that two regression lines were obtained having slopes of 0.624 and 0.665 for isothermal and heat transfer conditions, respectively. Both lines lie above the Eisenberg correlation line for a smooth cylinder. This suggests that enhanced mass transfer caused by surface roughness could explain the skewing of the data to higher values of the Sherwood number. Many workers2-9 agree that the surface roughness enhances the mass transfer and shifts the mass transfer correlation of Eisenberg et al1 to higher Sherwood numbers.

Table (1) shows that the range of exponent "b" is between (0.6-1.0). Poulson and Robinson7 stated that exponent "b" varies between (0.5-1.0) for most geometries and they obtained a value of 0.82. In the present work the "b" value for isothermal conditions is 0.624. This is in excellent agreement with that reported by Vilambi and Chin8, and it is also comparable to those obtained by other investigators1-3.

The value of the constant "a" depends on the mass transfer coefficient, diffusion coefficient of the relevant species and the kinematic viscosity of the solution (since it is the intercept of Sh/Sc0.356). It is worth to mention that the appreciable variability of the constant "a" (see Table (1)) can be attributed to the lack of certainty of the degree of saturation of the solution with oxygen from the air. Moreover the theoretical analysis of the Sherwood number depends on the difference in oxygen concentration between the bulk solution and the solution at the metal interface. The interfacial concentration is assumed to be zero or at least negligible relative to the concentration in the bulk solution. Thus, a 10% discrepancy in oxygen concentration will result in a 10% discrepancy in the Sherwood number2. Therefore, the agreement between the results obtained by Cornet and Kappesser2, Vilambi and Chin8, Sameh9 and the present work is most satisfactory.

The mass transfer correlation under heat transfer conditions (see Eq. (9)) also confirms the above discussion. However, the exponent "b" , under heat transfer conditions, is slightly greater than that obtained under isothermal conditions. This can be attributed to the existence of a temperature gradient between the electrolyte and the electrode surface under heat transfer conditions.13 This will distrub the viscous boundary layer and so the local increase in the turbulent intensity will enhance the mass transfer rate. Similar effects have been reported, previously, with the mass transfer process under laminar flow conditions.16,17 .

Figure (1) shows that the isothermal data are higher than those for heat transfer conditions. This can be explained as follows: At any bulk temperature and flow rate the mass transfer coefficient for heat transfer conditions is higher than that for isothermal conditions (see Tables 2 and 3). This increase in mass transfer coefficient is offset by the large increase in oxygen diffusion coefficient "D" , (see Eq. 3.C) due to interfacial temperature effect, The oxygen diffusion coefficient almost doubles for every 20K rise in temperature.

Conclusions

Mass transfer correlations for iron RCE in chloride / sulphate solution, under isothermal and controlled heat transfer conditions, were derived, i.e.,

$Sh = 0.307\, Re^{0.624}\, Sc^{0.356}$ (for isothermal conditions)

And

$Sh = 0.159\, Re^{0.665}\, Sc^{0.356}$ (for heat transfer conditions)

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Table 1: Some Correlations For Rotating Cylinder Electrode

Originator	Correlation	Temp., K	Experimental Conditions
Eisenberg et al[1]	$Sh = 0.079Re^{0.7}Sc^{0.356}$	298	Ferri-Ferro-Cyanide in alkaline solution, $10^3<Re<10^5$ $835 < Sc < 11490$
Cornet & Kappesser[2]	$Sh= 0.11\ Re^{0.64}$	296	4% NaCl aqueous solution $Sc=450$
Gabe & Robinson[3]	$Sh=0.079\ Re^{0.69}\ Sc^{0.4}$		$2900 < Re < 338800$ $830 < Sc < 2210$
Kishinevskii et al[4]	$Sh=0.033\ Re^{0.875}\ Sc^{0.013}$		$3.2 \times 10^5 < Re < 5.2 \times 10^5$
Kappesser et al [5]	$Sh= [1.25+5.79\log_{10}(d/\Sigma]^{-2}\ ReSc^{0.356}$		
Gabe & Walsh[6]	$Sh=0.079\ Re^{0.9}$	333	Copper plated steel.
Poulson & Robinson[7]	$Sh=0.026\ Re^{0.82}Sc^{0.33}$	323	Copper in dilute HC1 containing ferric ions
Vilambi & Chin[8]	$Sh=0.2\ Re^{0.61}$	296	Ferri-Ferro-cyanide in alkaline solution, $800 < Re < 80000$ $Sc = 1900$
Sameh[9]	$Sh=0.203\ Re^{0.82}\ Sc^{0.356}$	303	Carbon Steel cylinder in chloride solution ,$14000 < Re < 160,000$ $140 < Sc < 306$

Table (2) : Mass Transfer Coefficient, m/s x 10^5

rpm	Bulk Temperature, K		
	303	313	323
100	5.055	6.476	7.902
200	7.067	9.648	11.088
400	10.686	14.321	18.497
500	12.749	17.565	22.280

Table (3) : Sherwood Number

rpm	Bulk Temperature, K		
	303	313	323
100	1620	1611	1550
200	2265	2401	2176
400	3425	3563	3629
500	4086	4371	4371

Table (4) : Mass Transfer Coefficient Under Heat Transfer Conditions, m/s x 10^5

rpm	Bulk Temperature, K		
	303	313	323
100	5.328 (328.5)	6.716 (340.5)	8.355 (346.9)
200	7.775 (325.5)	9.455 (338.2)	11.321 (344.6)
400	11.637 (324.3)	16.171 (336.7)	18.446 (342.8)
500	13.901 (323.4)	20.112 (335.6)	21.865 (341.8)

Table (5) : Sherwood Number Under Heat Transfer Conditions.

rpm	Bulk Temperature, K		
	303	313	323
100	1240 (328.5)	1217 (340.5)	1246 (346.9)
200	1873 (325.5)	1752 (338.2)	1738 (344.6)
400	2849 (324.3)	3047 (336.7)	2910 (342.8)
500	3440 (323.4	3837 (335.6)	3489 (341.8)

Tables (6.a-c): Re, Sc, $Sc^{0.356}$, $Sh/Sc^{0.356}$ Under Isothermal Conditions

Table (6.a): at $T_b = 303$ K

rpm	Re, vd / γ	Sc γ / D	$Sc^{0.356}$	Sh	$Sh/Sc^{0.356}$
100	30697	375.88	8.255	1620	196.24
200	61393	375.88	8.255	2265	274.37
400	121934	375.88	8.255	3425	414.90
500	152630	375.88	8.255	4086	494.97

Table (6.b): at $T_b = 313$ K

rpm	Re vd/γ	Sc γ/D	$Sc^{0.356}$	Sh	Sh /$Sc^{0.356}$
100	37368	239.71	7.033	1611	229.06
200	74736	239.71	7.033	2401	431.39
400	148433	239.71	7.033	3563	506.61
500	185801	239.71	7.033	4371	621.50

Table (6.c) : at $T_b = 323$ K

rpm	Re,vd/γ	Sc, γ/D	$Sc^{0.356}$	Sh	Sh /$Sc^{0.356}$
100	44383	159.15	6.079	1550	254.98
200	88795	159.15	6.079	2176	357.95
400	176298	159.15	6.079	3629	596.97
500	220681	159.15	6.079	4371	719.20

Tables (7.a-c): R_e , Sc, $Sc^{0.356}$ Sh/$Sc^{0.356}$ Under Heat Transfer Conditions

Table (7.a) : at $T_b = 303$ K

rpm	Re, vd/γ	Sc, γ/D	$Sc^{0.356}$	Sh	Sh /$Sc^{0.356}$
100	39278	213.29	6.75	1240	183.70
200	76479	226.81	6.90	1873	271.45
400	150260	232.98	6.96	2849	409.34
500	186367	237.68	7.01	3440	490.73

Table (7.b) at $T_b = 313$ K

rpm	Re, vd/γ	Sc γ/D	$Sc^{0.356}$	Sh	Sh /$Sc^{0.356}$
100	47013	138.73	5.79	1217	210.19
200	92436	144.37	5.87	1752	298.47
400	181544	148.41	5.93	3047	513.83
500	225566	151.40	5.97	3837	642.71

Table (7.c) at $T_b = 323$ K

rpm	Re, vd/γ	Sc γ/D	$Sc^{0.356}$	Sh	Sh /$Sc^{0.356}$
100	53336	100.65	5.16	1246	241.47
200	105077	105.17	5.25	1738	331.05
400	205619	109.70	5.32	2910	546.99
500	255234	111.92	5.36	3489	650.93

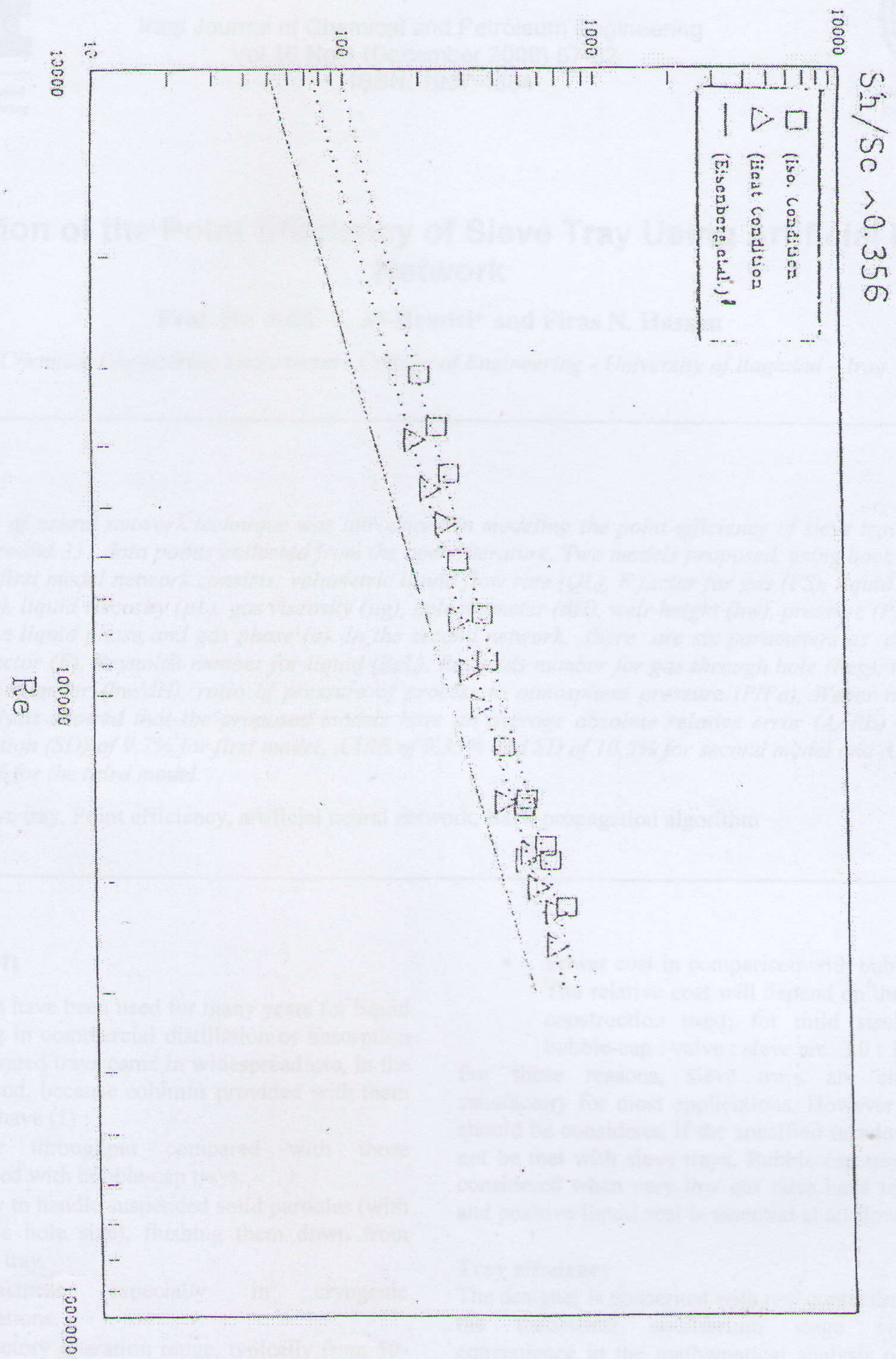

Fig.(1) :Sherwood Number-Reynolds Number Relationship Compared to the Eisen.,etal. Correlation (1)