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DIFFUSIVITY OF OXYGEN IN A NON-NEWTONIAN SALINE SOLUTION

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Abstract—The mass transport of oxygen to a rotating disc has been measured in a non-Newtonian saline solution using electrochemical polarization techniques. The diffusivity has been obtained from a comparison of the experimental results with the theoretical expression for the mass flux of Hansford and Litt. Results are presented for Polyox WSR301 concentrations varying from 0 to 10 000 parts per million by weight.

INTRODUCTION

THERE have been many studies that have dealt with the determination of the diffusivity in non-Newtonian systems. In one of the earliest studies, Clough *et al.* [1] pumped non-Newtonian liquids in laminar flow through tubes that were made of the diffusing solute. Measurements were taken of the total solution rate of β-naphthol in aqueous carboxymethyl-cellulose solutions and benzoic acid in slurries. The diffusivity was then determined from the Graetz–Leveque solution modified for non-Newtonian laminar flow [2, 3].

Astarita [4] measured the absorption of two gases, carbon dioxide (CO_2) and ethane (C_2H_4), in a number of non-Newtonian liquids. The diffusivity was calculated from an equation for absorption in ideal laminar cylindrical jets. In another experiment Astarita [5] measured the dissolution of slabs of benzoic acid into a falling film of aqueous carboxymethylcellulose. The results, when compared with theoretical results for non-Newtonian systems [5, 6], yielded a value for the diffusivity.

Hansford and Litt [7] considered the mass transfer from a rotating disc made of the solute diffusing to non-Newtonian solutions. They measured the rates of dissolution of benzoic acid and β-naphthol into an aqueous solution of carboxymethylcellulose, and of benzoic acid into aqueous polyethylene oxide. The value of the diffusivity was determined from the theoretical expression for the mass flux to a non-Newtonian liquid.

The present investigation is concerned with the determination of the molecular diffusivity of oxygen in aqueous sodium chloride solutions which are rendered non-Newtonian by addition of various concentrations of Polyox WSR 301 (Union Carbide), a completely water soluble polymer of ethylene oxide.

EXPERIMENTAL SYSTEM

A detailed description of the experimental system is available elsewhere (Ellison [8]). Briefly, the basic apparatus consisted of a disc that was mounted in the vertical plane and rotated about its horizontal axis in a pressure vessel that held the prescribed fluid (see Fig. 1). The fluid consisted of 4 per cent aqueous NaCl plus the additive Polyox WSR 301. The disc, 24·8 cm dia. and made of monel 400, was made cathodic while the anode was a titanium disc with platinum strips that was bolted to the back end of the vessel (Fig. 1). The reference electrode was 99·99% silver–silver chloride and was located 2·5 cm from the disc on the disc axis. The concentration of the oxygen in solution was determined by Winkler analysis.

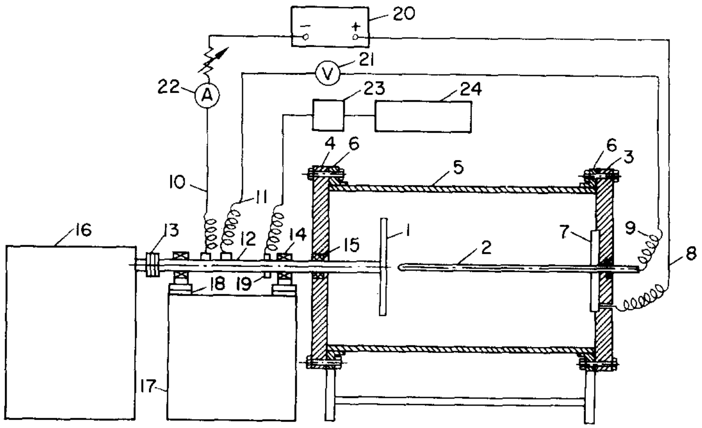

FIG. 1. Schematic diagram of the system (disc insulated at edge and back).

KEY

1. Disk
2. Ag–AgCl reference electrode
3. Back head (ASA 250 lb standard blind flange)
4. Front head (ASA 250 lb standard blind flange)
5. Shell (24 in. dia. 1/2 in. wall SA-53)
6. 2—ASA 250 lb standard slip-on welding flanges
7. Platinum titanium anode
8. Anode lead wire (insulated from head)
9. Probe lead wire
10. Current supply
11. Potential measuring contact
12. Shaft
13. Insulating coupling
14. 2—Bearings
15. Packing gland
16. 15 hp motor varidrive
17. Bearing support table
18. Insulating block
19. 60-tooth gear and induction pickup
20. Regulated power supply
21. High impedance voltmeter (Hewlett Packard 412A)
22. Ammeter (Western 430)
23. Pulse amplifier
24. Counter

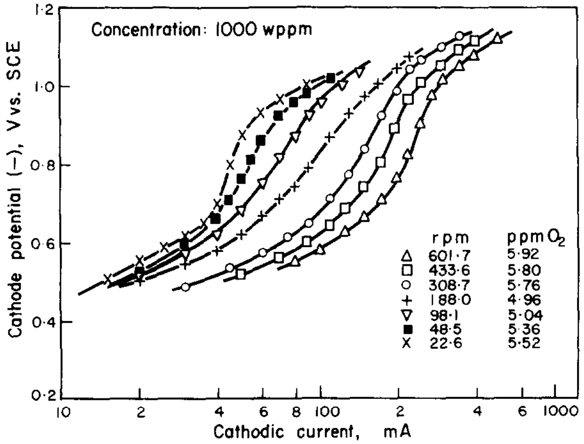

FIG. 2. Polarization curves.

DISCUSSION AND RESULTS

The transfer of oxygen, which is dissolved in the fluid, to the disc is accompanied by the liberation of electrons from the metal, this being responsible for the corrosion current. Thus, in systems where cathodic polarization controls the corrosion rate, the mass flux of the oxygen to the surface of the metals is directly related to the corrosion current. In cathodic protection, electrical current (from a battery, rectifier, or D.C. generator) supplies the electrons which reduce the oxygen at the surface, and the metal is polarized to a protected potential. When enough current is supplied so that the oxygen concentration at the surface approaches zero, the current–potential curve shows an inflection and the resulting current is called the mass

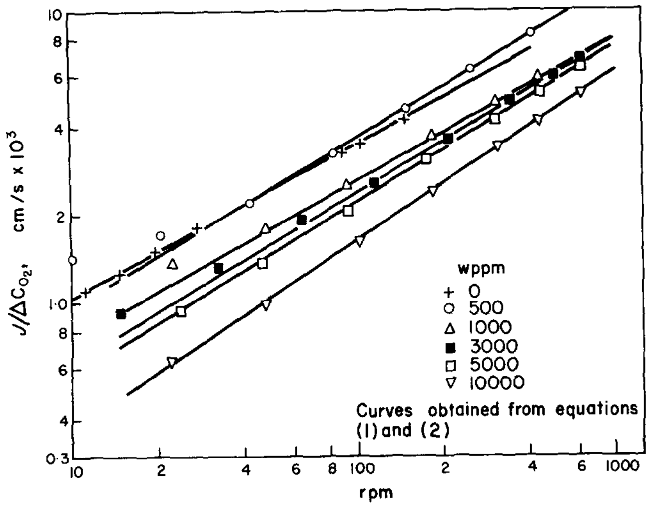

FIG. 3. Mass-transfer results for several concentrations of polyethylene oxide in 4% NaCl solution.

transfer limiting current. This corresponds to the maximum rate of mass transfer of oxygen and is ideally characterized by an infinite value of the concentration potential, i.e. an infinite slope of the polarization curve. Typical polarization curves are presented in Fig. 2 where the abscissa is the current between the anode and the cathode and the ordinate is the potential with respect to the reference electrode. The limiting current is chosen to be that current corresponding to the maximum, but finite, value of the slope [9–15].

The basic data is presented in Fig. 3 where the average mass-transfer coefficient, $J/\Delta C_{O_2}$, is plotted *vs*. the angular velocity of the disc for several concentrations of Polyox WSR 301. In the absence of Polyox, the results for transport in laminar flow to a rotating disc are well known [16, 17]. Indeed, the present apparatus was previously used for such studies and good agreement between the experimental and theoretical results was obtained (Ellison [8], Ellison and Cornet [18]).

For non-Newtonian fluids with high values of the Schmidt number, Hansford and Litt [7] present the following theoretical expression for the average mass-transfer coefficient:

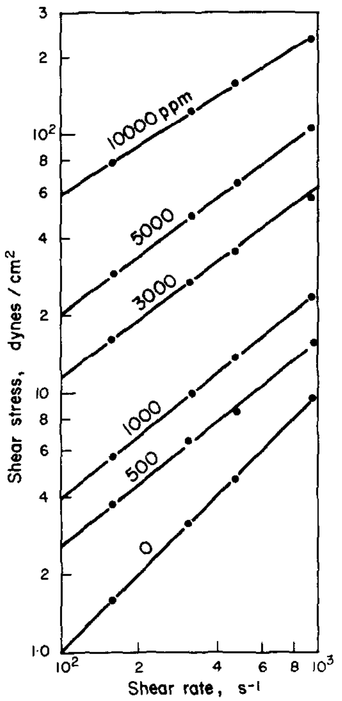

FIG. 4. Viscometric properties of polyethylene oxide in 4% NaCl solution.

$$\frac{J}{\Delta C_{O_2}} = \frac{\phi(n)}{0{\cdot}89}\frac{D}{R}\left[\frac{K}{\rho}\frac{\omega^{(n-1)}}{D}\right]^{\frac{1}{3}}\left[\frac{R^2\omega^{2-n}}{K/\rho}\right]^{\frac{(n+2)}{3(n+1)}} \tag{1}$$

where $\phi(n)$ is obtained from the solution of the conservation equations and is tabulated in [7]. For the pure saline solution, the effect of the lower Schmidt number was accounted for by using the procedure reported by Newman [19]. The parameters K and n arise from the use of the power-law model

$$\tau_{xy} = -K\left(\frac{dv_x}{dy}\right)^n. \tag{2}$$

They were obtained experimentally from measurements that were made in a Fann U-G, Model 35, rotating cylinder viscometer. The resulting shear stress-shear rate curves are shown in Fig. 4 for various mixtures of Polyox WSR 301 and 4% NaCl-H_2O solutions. The values for K and n are tabulated in Table 1.

Table 1. Viscometric properties of polyethylene oxide in 4% NaCl solution

Concentration of Polyox (wppm)	K	n
0	0·0094	1·00
500	0·062	0·81
1000	0·104	0·80
3000	0·50	0·69
5000	1·03	0·64
10000	4·50	0·55

The use of the theoretical relation for the average mass-transfer coefficient, equation (1) in conjunction with the experimental measurements allows one to determine a value for the diffusivity, D. The results for the diffusivities are presented in Table 2 for different concentrations of Polyox WSR 301, and the corresponding curves for the average mass-transfer coefficient are shown in Fig. 3. The agreement between the experimental and theoretical results is seen to be very good. It should be emphasized that the slope of the curves in Fig. 3 is a function of n[cf. equation (2)] which is determined *a priori* from the viscometer measurements. In detail, $J/\Delta C_{O_2}$ varies with rpm according to $(\text{rpm})^{1/(n+1)}$.

We note that runs at the different concentrations were also carried out at different temperatures. To account for this variation, the results for the diffusion coefficient, D, were divided by the diffusion coefficient of oxygen in saline solution, $D_{O_2,\,\text{saline solution}}$ at the temperature of the experiment and this ratio is also presented in Table 2. Note that the specific value of $D_{O_2,\,\text{saline solution}}$ of $2{\cdot}28 \times 10^{-5}\,\text{cm}^2/\text{s}$ which we obtained at a temperature of 75°F is in excellent agreement with the value interpolated from the data for saline solutions reported in the International Critical Tables [20]. The result of decreasing values for the diffusion coefficient, D, with respect to increasing concentration is consistent with the results obtained by Hansford and Litt [7] for benzoic acid in aqueous solutions of carboxymethylcellulose.

Table 2. Tabulation of diffusivities as obtained from mass-transfer results

Concentration of Polyox (wppm)	Temp (°F)	$D(\text{cm}^2/\text{s}) \times 10^5$	$D_{O_2,\,\text{saline solution}}(\text{cm}^2/\text{s} \times 10^5$	$D/D_{O_2,\,\text{saline solution}}$
0	75	2·28	2·28	1·00
500	90	2·68	2·80	0·96
1000	77	1·83	2·34	0·79
3000	79	1·79	2·40	0·75
5000	80	1·78	2·43	0·73
10000	83	1·49	2·55	0·58

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DIFFUSIVITÉ DE L'OXYGÈNE DANS UNE SOLUTION SALINE NON NEWTONIENNE

Résumé—Le transfert massique de l'oxygène à un disque tournant a été mesuré dans une solution saline non newtonienne en utilisant les techniques életrochimiques. La diffusivité a été obtenue à partir d'une comparaison des résultats expérimentaux et de l'expression théorique du flux massique donnée par Hansford et Litt. On présente les résultats obtenus pour des concentrations en Polyox WSR 301 variant de 0 à 10.000 p.p.m. en poids.

DIFFUSION VON SAUERSTOFF IN EINER NICHT-NEWTONISCHEN SALZLÖSUNG

Zusammenfassung—Es wurde der Massentransport von Sauerstoff an eine rotierende Scheibe in einer nicht-Newtonischen Salzlösung mit Hilfe elektrochemischer Polarisationstechniken gemessen. Der Diffusionskoeffizient wurde durch Vergleich der experimentellen Ergebnisse mit dem theoretischen Ausdruck für den Massenstrom (nach Handford und Litt) ermittelt. Ergebnisse werden mitgeteilt für Konzentrationen an Polyox WSR 301 im Bereich von 0 bis 10 000 ppm (Masse).

КОЭФФИЦИЕНТ ДИФФУЗИИ КИСЛОРОДА В НЕНЬЮТОНОВСКОМ СОЛЯНОМ РАСТВОРЕ

Аннотация—Используя электрохимическую методику поляризации, измерялся перенос массы кислорода к вращающемуся диску в неньютоновском соляном растворе. Коэффициент диффузии найден на основе сравнения экспериментальных результатов с теоретическим выражением Хэнсфорда и Литта для массового потока. Результаты представлены для концентраций полиокса, изменяющихся от 0 до 10 000 весовых частей на миллион.