

STUDIES ON THE REDOXOKINETIC EFFECT: PREPARATION OF REPRODUCIBLE ELECTRODE SURFACES*

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ABSTRACT

An experimental technique has been developed for obtaining a reproducible platinum electrode surface for measurement of the redoxokinetic potential. The values for ψ for the platinum/ferrous sulphate-ferric sulphate-sulphuric acid system at room temperature are reported, at frequencies of the A.C. field within the range 50–250 cycles/second. The energy transfer coefficient has been calculated from the measurements of ψ .

The effects of the circuit resistance, frequencies within the range 50–250 cycles/second and of temperature on the value of ψ have been studied and the results discussed in relation to the theory of the redoxokinetic effect.

1. INTRODUCTION

WHEN an alternating electric field is made incident on two platinum electrodes dipped in an aqueous solution containing a reversible redox system, it is found that a D.C. potential is developed at each of the electrodes, which can be measured with reference to a third platinum electrode dipped in the same solution.¹ This phenomenon has been called the redoxokinetic effect, since it is produced by the kinetics of the reduction-oxidation processes at the electrodes. The D.C. potential developed is termed the redoxokinetic potential. The theory of the redoxokinetic effect has been worked out,² applying the theory of electromotive force as proposed by Glasstone, Laidler and Eyring,³ for the particular case of small fields and corresponding to equal concentrations and diffusion coefficients of the oxidant and the reductant. A more generalised treatment has been given by G. C. Barker,⁴ whose final equations reduce to those of Doss and Agarwal for

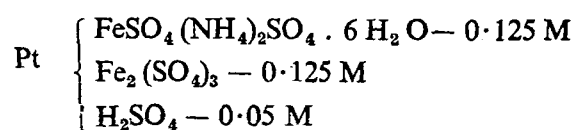
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the particular conditions assumed by the latter. The predictions of the theory have all been amply verified by the work of Doss and Agarwal and of Barker. The latter by making an ingenious combination of theoretical principles and experimental techniques has demonstrated how the redoxokinetic effect (*a*) is a unique tool for studying the kinetics of fast electrode reactions and (*b*) has given rise to the development of the new and powerful analytical technique, RF polarography.

The redoxokinetic measurements have enabled the measurement of α , the energy transfer coefficient. This has been done so far with mercury/aqueous interfaces. For platinum/aqueous interfaces, however, Doss and Agarwal have reported that the value of α calculated from the values of ψ measured by them was not reproducible.² In discussing this, they have drawn attention to the importance of the previous history of the platinum electrode for obtaining reproducible values of α . An attempt is made in the present work to examine the conditions under which reproducible surface can be obtained for the determination of α .

2. EXPERIMENTAL

The circuit diagram of the experimental arrangement used is given in Fig. 1. The A.C. source was stabilized by the use of a baretter. The alternating field present at the electrode was measured by means of a Philips Vacuum Tube Voltmeter (Type GM 6015) using a range of 0–30 mV. r.m.s. with an accuracy of 1–2%. The redoxokinetic potential was measured by a Leeds and Northrup Galvanometer with a resistance of 54.4 k.ohms (including the critical damping resistance). The sensitivity of the galvanometer under these conditions was 6.67 microvolt per mm. deflection. The system studied was:



The chemicals used were of A.R. grade.

3. RESULTS

Flaming the platinum electrodes was the first technique studied for obtaining a reproducible surface. A typical set of measurements is recorded in Table I. The redoxokinetic potential varied with time and it took considerable time to get a steady value. The steady value obtained was also not constant, but varied largely with platinum wires of different thicknesses and even with the same platinum wire in different experiments.

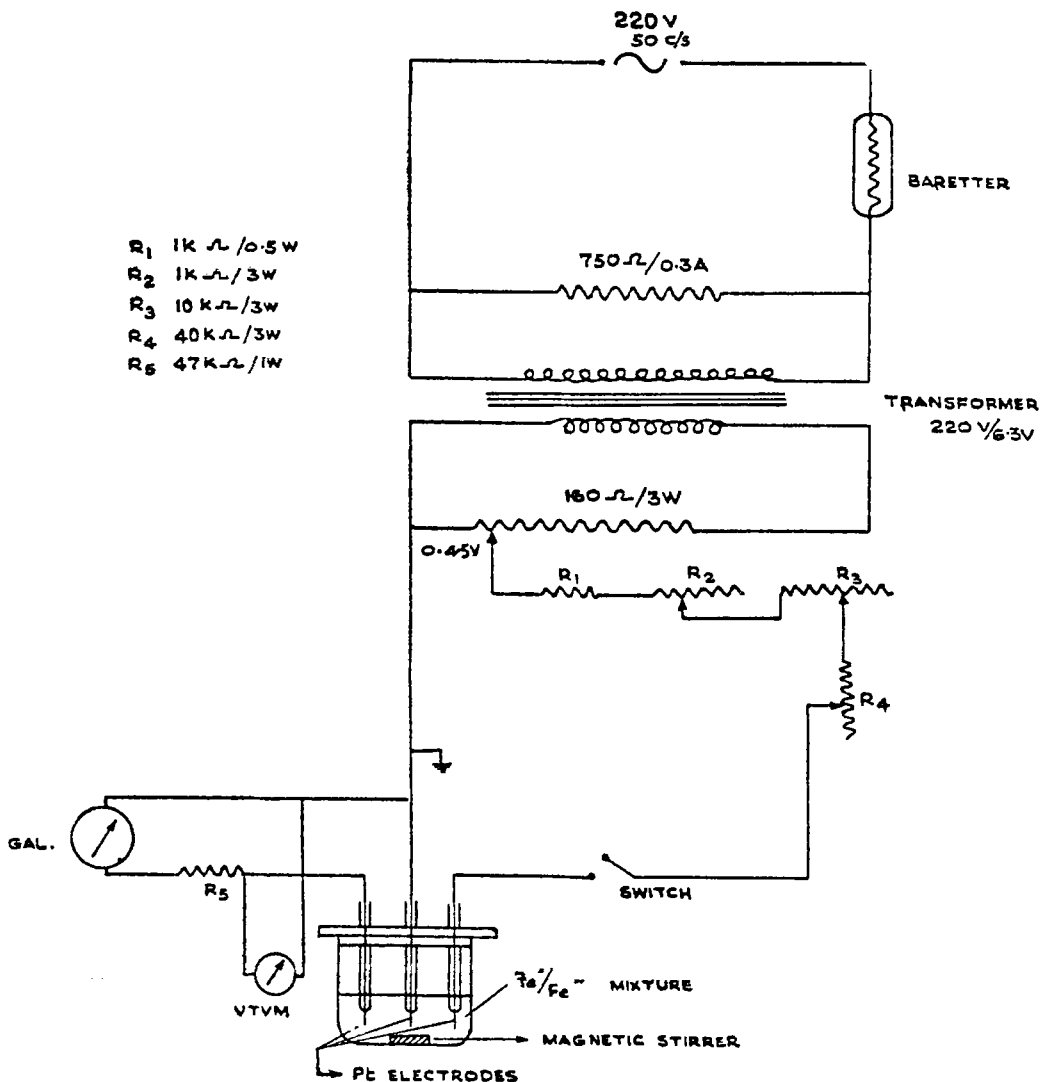


FIG. 1

The addition of amyl alcohol in large quantities to the electrolyte reduced the variation in the values of the redoxkinetic potential and led to an increase in its magnitude (Table II). In subsequent experiments, however, the addition of amyl alcohol was avoided, as the intention was to study a system free from extraneous substances.

A number of other techniques for getting a reproducible surface were examined and it was found that the following sequence of treatment gave

TABLE I

Redoxokinetic potential at flamed electrodes[Electrode size: 0.3 mm. diameter \times 6.4 mm. length; A.C. Potential: 20 mV. (r.m.s.)]

Expt. No.	Redoxokinetic potential in microvolts		
	Time (in minutes)		
	1	5	10
1	360	427	467
2	680	700	754
3	260	420	600
4	434	400	446
5	387	474	534
6	100	414	560

TABLE II

Effect of addition of amyl alcohol

[A.C. Potential: 20 mV. (r.m.s.); measurements taken at 1 min. after immersion of the electrodes in solution containing a layer of amyl alcohol]

Size of electrode	Treatment of electrode if any	ψ in microvolts			
		1	Experimental No. 2	3	4
0.5 mm. diameter \times 25.4 mm. length	Flamed	407	454	374	347
Do.	Not flamed	323	374	467	400
0.25 mm. diameter \times 6.4 mm. length	Flamed	534	620	434	510
Do.	Not flamed	897	914	854	850

the best reproducibility. The platinum surface was immersed in hot chromic acid (90° C.) for 5 minutes and, after washing with distilled water, was treated with concentrated hydrochloric acid for 1 minute, washed with water and immersed for 5 minutes in boiling ferrous-ferric mixture of the same composition as the electrolyte used in these experiments. Even this treatment did not give concordant values for the redoxokinetic potential with platinum electrodes of different sizes (*vide* Tables III and IV). Immersion of the platinum wire in the boiling ferrous-ferric mixture for 30 minutes gave a surface which had the best reproducibility so far obtained by us and gave concordant values with platinum wires of different thicknesses. It may also be noted that the purpose in using wires of different

TABLE III

Effect of treatment of electrode surface

[Electrodes immersed in chromic acid at 90° C. (for 5 minutes) concentrated HCl and boiling ferrous-ferric solution (for 5 minutes); A.C. potential: 20 mV. (r.m.s.); electrolyte stirred magnetically]

Size of electrode	Time after immersion of electrode (in minutes)	ψ in micro volts					
		Experimental No.					
		1	2	3	4	5	6
0.25 mm. diameter × 6.4 mm. length	1	1311	1311	1300	1277	1401	1323
Do.	5	1344	1256	1207	1294	1408	1374
0.5 mm. diameter × 6.4 mm. length	1	1256	1000.5	934	987	971	981
Do.	5	1243	1001	900	967	951	957
0.75 mm. diameter × 6.4 mm. length	1	1167	1161	1250	1268	1221	1214
Do.	5	1174	1140	1174	1248	1207	1194

thicknesses was mainly to examine the variation in the redoxokinetic effect with different lots of platinum wire.

TABLE IV

Effect of treatment of electrode surface

(Experimental conditions same as for Table III except for time of immersion of electrodes in boiling ferrous-ferric mixture which was 30 minutes)

Size of electrode	Time after immersion (in minutes)	ψ in microvolts			
		Experiment No.			
		1	2	3	4
0.25 mm. diameter \times 6.4 mm. length	1	1360	1261	1207	1308
Do.	5	1397	1280	1234	1294
0.5 mm. diameter \times 6.4 mm. length	1	1243	1248	1268	1243
Do.	5	1248	1256	1268	1234
0.75 mm. diameter \times 6.4 mm. length	1	1174	1380	1428	1261
Do.	5	1167	1380	1428	1261

Other important observations made in the course of these experiments were—(1) the arrangement of the three electrodes had no effect on the value of the redoxokinetic potential provided the reference electrode was in a line with the other 2 electrodes and at a sufficient distance from them; (2) the redoxokinetic effect could be measured with only two electrodes, if of them was a gauze electrode of large surface surrounding the other electrode.

The effect of the circuit resistance on the redoxokinetic potential was negligible within the limits of experimental error as may be seen from the readings in Table V.

The effect of frequency was examined using an audio oscillator giving 200 and 250 cycles/second in place of the 50 cycles source. The results showed that the redoxokinetic effect of the ferrous-ferric system studied

TABLE V

Effect of circuit resistance on the redoxkinetic potential

[Treated electrodes: 0.5 mm. diameter \times 6.4 mm. length; A.C. potential: 20 mV. (r.m.s.); measured by balancing against a potentiometer]

Resistance of the circuit in $K \Omega$	ψ in microvolts	
	Experiment No.	
	1	2
54.4 (normal circuit)	900	855
109.9	905	855
162.4	893	860
219.9	913	850
269.9	890	855
337.4	910	850
537.4	910	860
1007.4	920	865

TABLE VI

Effect of frequency

[Treated electrodes: A.C. potential 20 mV. (r.m.s.)]

Size of electrode	Frequency of A.C. field c./s.	ψ in microvolts
0.5 mm. diameter \times 6.4 mm. length	50	1527
Do.	200	1441
Do.	250	1428
0.75 mm. diameter \times 6.4 mm. length	50	1400
Do.	200	1347
Do.	250	1340

was not sensibly dependent on the frequencies within this range (Table VI). The effect of higher frequencies is under investigation.

Since the electrode reaction rate would rise with increase in temperature, it was of interest to study the effect of temperature. The redoxkinetic potentials measured at different temperatures are given in Table VII.

TABLE VII

Effect of temperature

[Treated electrodes of 0.5 mm. diameter \times 6.4 mm. length; A.C. potential: 20 mV. (r.m.s.)]

Temperature $^{\circ}$ C.	ψ in microvolts
33	1057
40	894
50	734
60	527
70	347
80	247
90	73

4. DISCUSSION

The variation in the value of the redoxkinetic potential measured at untreated platinum electrodes could be attributed to the history of the platinum wire, as already mentioned and also to the slow adsorption of surface-active substances from the solution on the platinum surface. The latter effect is confirmed by the results of the experiments using large quantities of amyl alcohol with the electrolyte. The failure of the technique of flaming to give a reproducible value for ψ is presumably due to the occlusion on the platinum surface of reducing or oxidising gases from the flame in an irreproducible manner. It is not, however, clear whether the reproducibility obtained by immersion of the platinum electrode in boiling ferrous-ferric mixture is due to a more rapid attainment of a definite redox state at the surface or to a more rapid attainment of equilibrium with regard to the adsorption of surface-active substances present in traces in the electro-

lyte solution or both. The redox state referred to here does not refer to the equilibrium potential since the redox potential itself reaches the equilibrium value in a very short time within about 10 microvolt irrespective of the previous history of the platinum electrode, whereas the redoxkinetic effect shows variations unless the electrodes are subjected to the treatment described. It is clear from this that the electrode kinetics is far more influenced by the surface conditions than the equilibrium values of potential. In this connection, it is of interest to note that any inert electrode would behave similarly to platinum with regard to the equilibrium values of the redox potential.

The observation that the circuit resistance is without effect on the redoxkinetic potential even when it is increased ten or twenty-fold shows that the measuring circuit is not drawing current to any significant extent in the present system and that extrapolation to infinite resistance is therefore unnecessary.

The redoxkinetic potential of this system is found to be independent of the frequency within the range 50–250 cycles/second. Assuming that the ψ has attained its limiting value for high frequencies, the value of α can be calculated from the values of ψ in Table IV by applying the equation

$$\psi = - (a - 0.5) \frac{V^2 n F}{2RT}.$$

The value comes out to be 0.4 ± 0.01 . Stirring at different rates and even the absence of stirring produced no change in the redoxkinetic potential, except that gentle stirring gave more reproducible results perhaps by speeding up the attainment of equilibrium.

It is to be pointed out, however, that the concentration of the indifferent electrolyte, namely H_2SO_4 in the system studied, was of the same order as that of the ferrous and ferric ions. Migration effects cannot therefore be ruled out, and the extent to which these might be influencing the value of ψ is under examination. The effect of higher frequencies is also under investigation.

The experiments on the effect of temperature show that the redoxkinetic potential decreases with rise in temperature and becomes practically zero at $90^\circ C$. This may be explained on the basis of the increase in 'k' at higher temperatures brought about by the diminished energy requirements for activating the ions. It is also possible that part of the variation might arise from variations in the value of ' α '.

