FARADAIC RECTIFICATION STUDY OF THE EFFECT OF NONPOLAR LIQUIDS ON THE TRANSFER COEFFICIENT AND KINETICS OF REDOX PROCESSES*

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The rectification of an alternating current by an electrode reaction, due to the asymmetry of its current–potential curve with respect to the equilibrium potential, is known as faradaic rectification (Oldham 1957 ; Barker 1958 ; Barker, Faircloth, and Gardner 1958). The application of faradaic rectification to the study of electrode kinetics has led to a convenient method (Matsuda and Delahay 1960) for the determination of the transfer coefficients and rate constants at equilibrium of fast electrode processes. Nonpolar liquids like benzene and toluene have been reported (Gupta 1953) to bring about changes in capacity at the dropping mercury electrode ; their effect on the electrode kinetics of the ferrous–ferric reaction has been studied in the present work.

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The method used for the measurement of ψ, the shift in mean potential, and of V, the alternating oltage superposed is the same as described earlier (Agarwal 1962, unpublished data). A saturated solution of the nonpolar liquid (A.R.) in $1N$ H_2SO_4 was prepared, so as to use it for preparing $0\cdot002M$ solution of each cation (Fe^{2+} and Fe^{3+}), by dissolving the calculated amounts of ferric and ferrous ammonium sulphates (A.R.). The nonpolar liquids used are benzene (A.R.) and toluene (A.R.). The observations were made at alternating voltages of 4 mV and of 8 mV to verify the variation of ψ with the square of the alternating voltage. As the values of ψ at 8 mV were found to be exactly four times those obtained at 4 mV, the values of ψ only at 4 mV are given in Table 1.

TABLE 1

DIMENSIONS OF BRIGHT, POLISHED PLATINUM FOIL ELECTRODES USED

A.C. electrodes :	Length (cm)	Breadth (cm)
1	$1\cdot30$	$1\cdot15$
2	$1\cdot30$	$1\cdot10$ (earthed)
Reference electrode :	$1\cdot30$	$1\cdot10$
Temp. of the thermostat : $35\pm0\cdot05$ °C		

Frequency (c/s) of A.C. used	Values of ψ (μV) at 4 mV of A.C. when Each Redox Concentration is $0\cdot002M$ in $1N$ H_2SO_4, Containing Saturated Soln. of :		Remark
	Benzene	Toluene	
50	-28	-22	For toluene, ψ de-
100	-38	-30	creases in magnitude
200	-52	-40	at the respective
500	-58	-56	frequency as com-
1000	-60	-56	pared to that of
2000	-60	-56	benzene

The diffusion coefficient of $0\cdot001M$ ferric ammonium sulphate in $1N$ H_2SO_4 containing a saturated solution of the nonpolar liquid was determined by the porous diaphragm cell method. The amount of ferric salt diffused at different intervals of time in the supporting electrolyte was determined by an electrochemical method, whose details have been discussed under a separate paper. The values of the concentration gradient and of the mean concentration for the diffusion of $0\cdot001M$ ferric salt in $1N$ H_2SO_4 containing benzene are given in Table 2.

From Table 1, it can be seen that ψ becomes constant at frequencies of 500 c/s and higher, when either of the nonpolar liquids is present. ψ is found to increase in magnitude when benzene is added to the redox couple as compared to the values of ψ obtained on addition of toluene. Therefore, α, the transfer coefficient, in the former case will be higher than in the latter. The values of α were calculated from the theoretical equation (Doss and Agarwal 1952) applicable at high frequency when ψ becomes constant, that is,

$$\alpha = 0\cdot5 - (2\psi RT/V^2 nF),$$

where R is the gas constant, T is the absolute temperature, V is the alternating voltage, n is the valency, and F is the Faraday. The values of the transfer coefficient thus determined are $0 \cdot 699$ when benzene is added to the redox couple and $0 \cdot 686$ when toluene is added instead. These values are higher than that obtained by Agarwal's (1962a) value of $0 \cdot 586$, with no addition of nonpolar liquid to the reactants.

To obtain information about the influence of nonpolar liquids on electrode kinetics, the diffusion coefficient of the reactants in the presence of benzene was calculated from the data given in Table 2, following the method adopted by Hartley and Runnicles (1938). The diffusion coefficient thus obtained is

TABLE 2

CONCENTRATION GRADIENTS AND MEAN CONCENTRATION FOR DIFFUSION OF $0 \cdot 001$M FERRIC AMMONIUM SULPHATE IN 1N H_2SO_4 CONTAINING SATURATED SOLUTION OF BENZENE

Ferric ammonium sulphate solution taken in compartment A of the porous diaphragm cell, 60 c.c. ; supporting electrolyte (s turated solution of benzene in 1N H_2SO_4) taken in compartment B of the porous diaphragm cell, 110 c.c. ; cell constant, $3 \cdot 46$; temp. of thermostat, $35 \pm 0 \cdot 05$ °C

Time t_1 (min)	Conc. Diffused Salt $C_1 \times 10^6$ (g-equiv/l)	Time t_2 (min)	Conc. Diffused Salt $C_2 \times 10^6$ (g-equiv/l)	Conc. Gradient $\dfrac{dc'}{dt} \times 10^6$	Mean Conc. $\overline{C} \times 10^6$
255	$17 \cdot 0$	663	$35 \cdot 1$	$0 \cdot 04$	$26 \cdot 0$
282	$19 \cdot 5$	635	$33 \cdot 5$	$0 \cdot 04$	$26 \cdot 5$
318	$23 \cdot 4$	606	$31 \cdot 6$	$0 \cdot 03$	$27 \cdot 5$
348	$25 \cdot 7$	576	$30 \cdot 2$	$0 \cdot 02$	$27 \cdot 9$
378	$26 \cdot 7$	548	$29 \cdot 5$	$0 \cdot 02$	$28 \cdot 1$
405	$27 \cdot 9$	520	$28 \cdot 5$	$0 \cdot 01$	$28 \cdot 2$
		Mean of first five :		$0 \cdot 03$	$27 \cdot 2$

$9 \cdot 4 \times 10^{-6}$ cm^2 sec^{-1} when benzene is added to the redox couple. A similar value is obtained, when instead of benzene, toluene is added to the system. The rate constant at equilibrium in the above case can be calculated (Agarwal 1962, unpublished data) by substituting ψ (at 4 mV and 50 c/s, from Table 1) and the value of the diffusion coefficient in the theoretical equation applicable at low frequency (Doss and Agarwal 1952), that is

$$K_s = (0 \cdot 5 - \alpha) \frac{V^2 nF}{4 \psi RT} \sqrt{(\tfrac{1}{2} \omega D)}.$$

The value of K_s thus obtained is $4 \cdot 1 \times 10^{-2}$ cm sec^{-1} in the presence of benzene. On addition of toluene to the ferrous–ferric redox system, the same order of value of the rate constant is obtained. On comparing the above value

with that of the ferrous–ferric redox couple (Agarwal 1962, unpublished data) without addition of any nonpolar liquids, $K_s = 4\cdot5 \times 10^{-2}$, it becomes evident that the addition of nonpolar liquid does not influence the rate constant appreciably.

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