Asian Journal of Chemistry Vol. I, No. 3 (1989), 273–281

Electrochemical Study of the Reduction of Manganese (III) by Rotating Disc Voltammetry in Non-aqueous Solvents

F. A. ABEED* and K. SH. AHMED

Chemistry Department, College of Science, University of Mosul, Mosul, Iraq.

The voltammetric behaviour of the Mn(III) has been examined at rotating disc electrodes of silver, gold and glassy carbon electrodes in dimethylforamide (DMF), acetonitrile (ACN), ethanol (EtOH) and methanol (MeOH). Cathodic reduction of Mn(III) displayed a single well-defined cathodic wave and obeyed the Levich plots at all electrodes and solvents studied. The limiting current is linearly proportional to concentration affording an excellent and rapid determination of Mn(III). The electrode kinetic parameters, conditional potentials have been determined and the effects of the solvents on these parameters have been explored.

INTRODUCTION

The electrode reaction of manganese (III)-manganese (II) has been widely used coulometrically. A number of papers have been published[1–4] on the electrochemical behaviour of Mn(III)/Mn(II) systems in aqueous solution. However, very few electrochemical studies have been made on this couple in non-aqueous solvents at rotating disc electrodes.[5] A full investigation was therefore undertaken of the voltammetry at rotating disc electrodes (RDEs) of silver, gold and glassy carbon in non-aqueous solvents, for electrode kinetics and analytical purposes.

EXPERIMENTAL

The purification of the solvents used has been described.[6–9] $Mn(Ac)_3$, $Mn(Ac)_2$ and lithium perchlorate were obtained from Fluka and used with out further purification.

Stock solutions of the substances studied were prepared by dissolving the precisely weighed amount of each substance in the solvent used.

All electrochemical measurements were carried out using a potentiostat of the type ST 72, supplied by Gerhard Bank Electronic. The wave form generator used was of the type R.B.2, supplied by chemical electronics. The voltammograms were recorded using 29000 A Braynas X-Y recorder.

A three-electrode cell was used; the working electrode was a rotating disc of the type- Brucker ERST with gold, silver and glassy carbon electrode. The reference electrode was a saturated calomel electrode (SCE);

and the counter was platinum plate. The normal voltammetric scan rate was 5 mV s^{-1} and the geometric area of the disc electrodes was 0.28 cm^2.

RESULTS AND DISCUSSION

Voltammetry

The current-potential curves for the reduction of manganese (III) were recorded at silver, gold and glassy carbon electrodes at different rotation speeds using scan speed of 5 mV s^{-1}. Figures (1–4) illustrate typical examples of the cathodic voltammograms, which clearly defined limiting currents were obtained at all three electrodes in dimethylformamide and acetonitrile, where as is less defined in ethanol and methanol. The Levich plots displayed excellent linearity with zero or near zero intercepts. From this it is clear that the electrode process is controlled by diffusion.

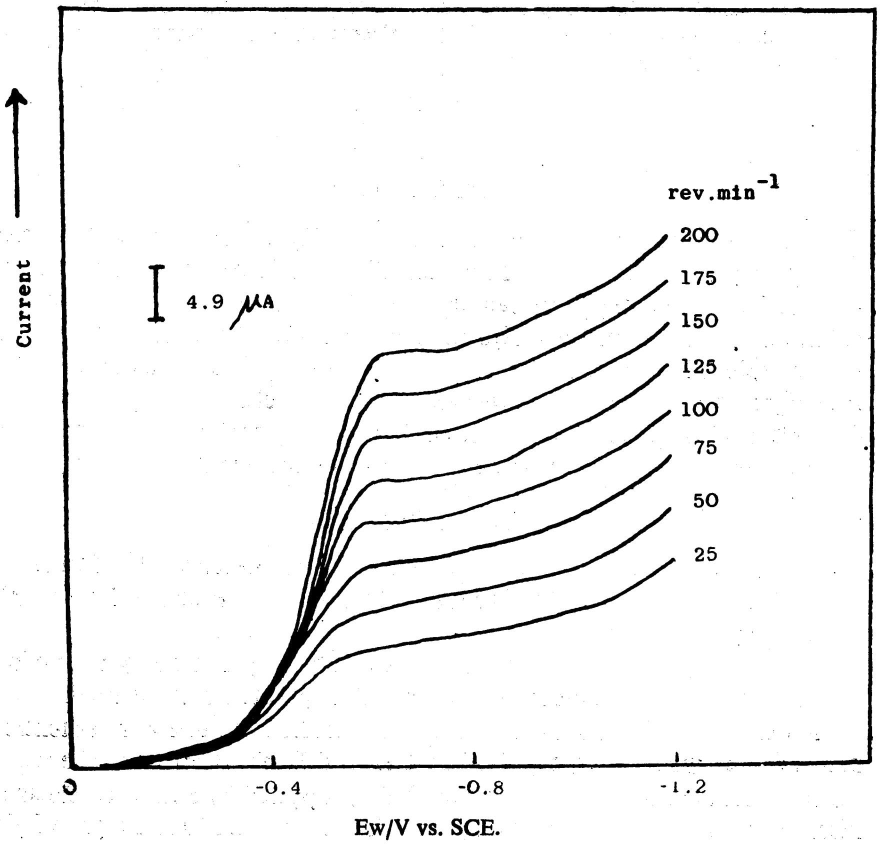

Fig. 1. Current-Potential graphs for the reduction of manganese (III) at gold rotating disc electrode in ACN solution: 10^{-3}M $Mn(AC)_3$ + 0.1M $LiClO_4$.

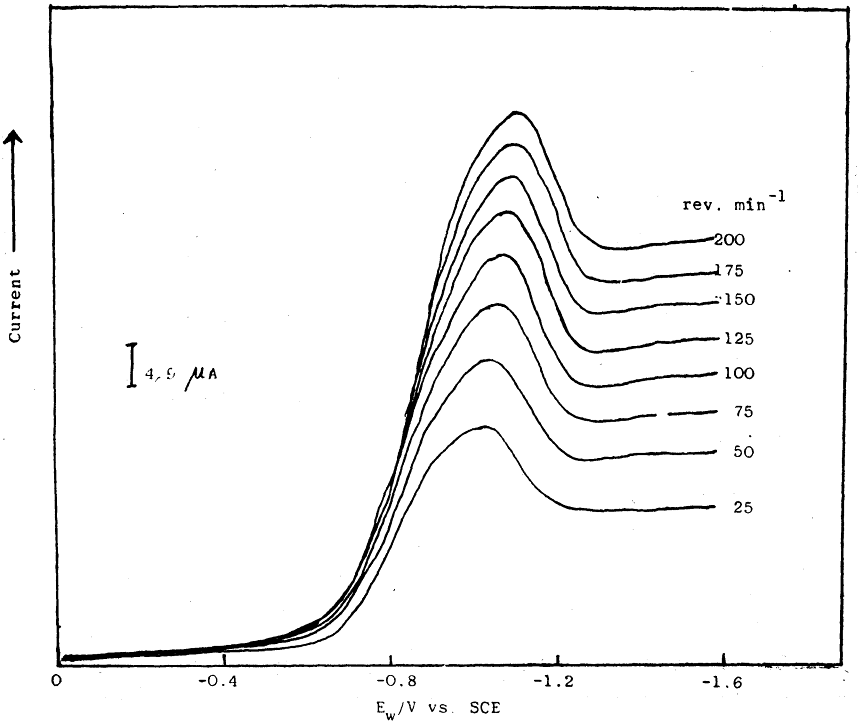

Fig. 2. Current-Potential graphs for the reduction of manganese (III) at glassy carbon rotating disc electrode in DMF solution: 10^{-3} M Mn $(AC)_3$ + 0.1M $LiClO_3$.

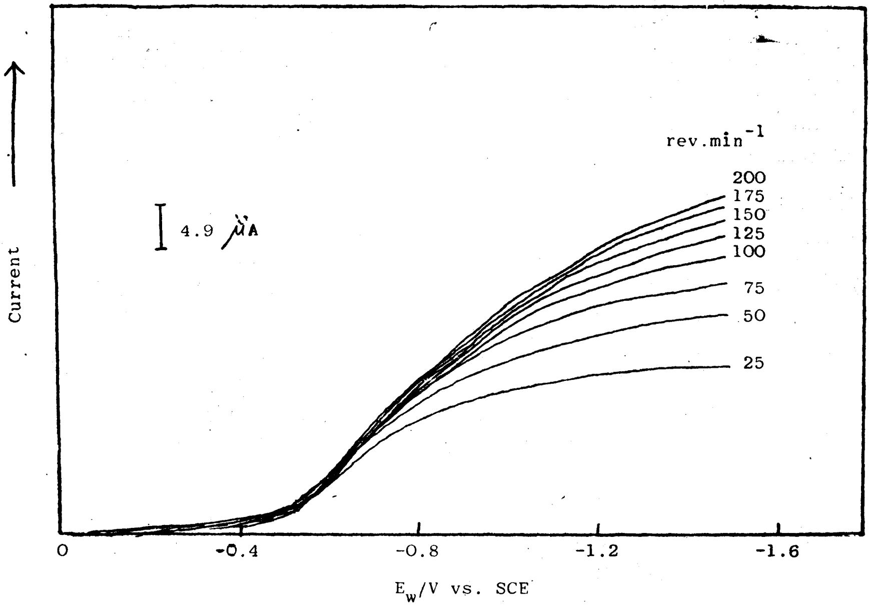

Fig. 3. Current-Potential graphs for the reduction of manganese (III) at silver rotating disc electrode in ethanol solution: 10^{-3}M $Mn(AC)_3$ + 0.1M $LiClO_4$.

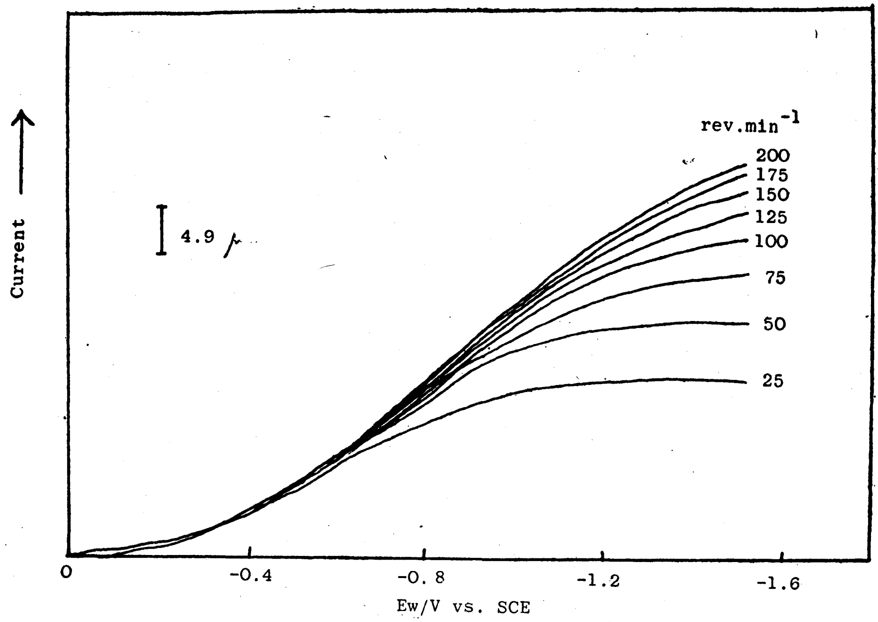

Fig. 4. Current-Potential graphs for the reduction of manganese at (III) glassy carbon rotating disc electrode in methanol. solution: 10^{-3} Mn (AC)$_3$ + 0.1M LiC10$_4$.

Figure (5) show examples of Levich plots.[10] A similar behaviour was found for the dependence of the limiting current on manganese (III) concentration (10^{-3}–10^{-6} M) in dimethylformamide and acetonitrile. This is also another evidence that the observed limiting current is a diffusion controlled limiting current. In ethanol and methanol the plot of limiting current versus concnetration displayed some curvature and non-zero intercepts.

Solvents Effect on Conditional Potentials

The conditional potentials for Mn(III)-Mn(II) couple were determined by single point measurement. A solution of equimolar concentration of Mn(III)-Mn(II) was prepared in the solvent studied, and the zero-current potentials were measured at three different electrode materials. Time was allowed for the attainment of a stable reading, until drift was less than 3 mV s^{-1}. Electrodes reached the stable reading within 4–5 minutes in dimethylformamide and acetonitrile, while took about 60 minutes in ethanol and methanol.

The values obtained in different solvents are summarised in Table 1 and comprised parameters that describe solvent properties. The conditional potentials found follow the sequence; glass carbon > gold > silver in all solvent studied. Moreover it was found that changing the solvent has

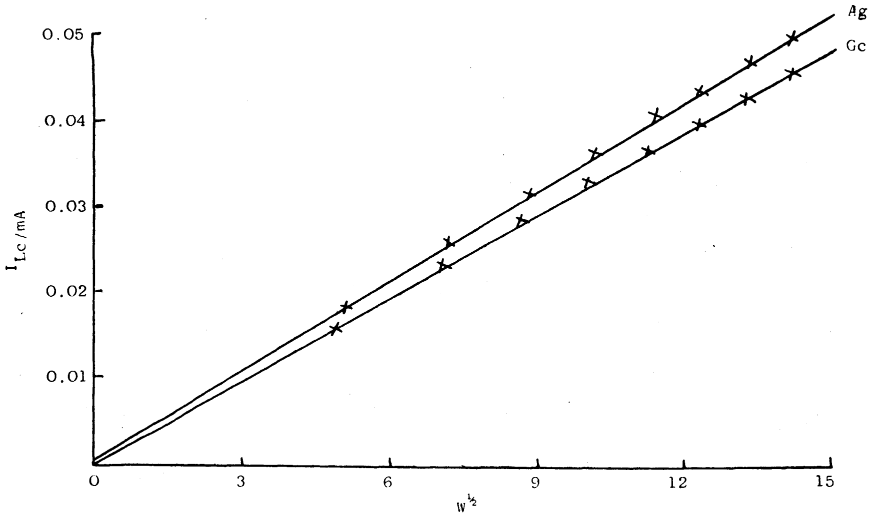

Fig. 5. Levich plots for reduction of manganese (III) in acetonitrile.

TABLE 1

CONDITIONAL POTENTIALS FOR Mn(III)/Mn(II) vs. SCE IN VARIOUS SOLVENTS

Solvent	Acceptor number[11]	Dielectric constant	E°′/volt		
			Au	Ag	GC
DMF	16	36.1	0.16	−0.05	0.20
ACN	18.9	32	0.34	0.17	0.39
EtOH	37.1	24.3	0.43	0.21	0.45
MeOH	41.3	32·6	0.45	0.24	0.48

significant influence on the conditional potentials, which decrease in the order MeOH > EeOH > ACN > DMF which is the same order of the acceptor number of the solvents. This variation could be due to different electron acceptor properties which has a great influence on the solvation of the cations. No correlation is found with the dielectric constant.

Kinetic parameters

The voltammograms obtained in the solvent studied can be described by simple mass transfer-charge transfer theory.[12,13] The main equations are

$$\frac{1}{i} = \frac{1}{I} + \frac{K}{W^{1/2}} \tag{1}$$

$$\text{Log}\, I = \text{Log}\, nFAC\, K^{\circ} - \frac{\alpha\, nF}{RT}(E - E^{\circ\prime}) \tag{2}$$

Where i A is the current for a particular electrode potential, W rad s^{-1} the RDE-rotational frequency, K the potential-dependent constant, I A the current corrected for diffusion, EV the electrode potential vs. SCE, E°′V the conditional potential vs. SCE, K° the conditional charge-transfer rate constand, ∝ the cathodic charge-transfer coefficient, A cm^2 the electrode surface area, C mol l^{-1} the bulk concentration of manganese (III) and n, F, R and T are as in the nernst equation. If equation (I) is applied to the set of voltammograms in Fig. 1. the plot of 1/i versus $1/w^{1/2}$ gives I from the intercept. A different value of I can be obtained for each electrode potential E, as illustrated in Fig. 6.

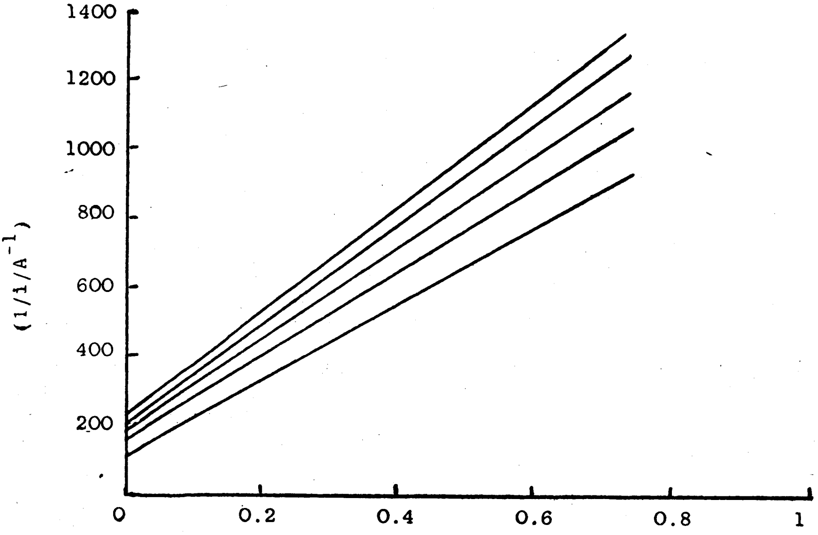

Fig. 6. Mass extrapolation-out graph following equation (1). Each line corresponds to a different electrode potential. Solution: 10^{-3}M $Mn(AC)_3$ + 0.1 $LiClO_4$' in acetonitrile at gold rotating disc electrode.

A graph of I versus E-E°′ using equation (2) gives a straight line. The charge-transfer kinetic parameters K° and ∝ are obtained from the intercept and slope and are given in Table 2. There is a little variation incharge transfer coefficients which range a round 0.32. The electrode material has marked effect on the manganese reaction rate; the K° sequence is glassy carbon > gold > silver in all solvents. On the other hand the values, obtained in various solvents are decrease in the sequence DMF > ACN > EtOH ≃ MeOH. This could be attributed to change in solvation sphere or the structure of the double layer of the solvents.[14,15] This indicates a higher activation energy of the reaction in EtOH and MeOH and consequently the reaction proceeds faster in DMF and ACN.

TABLE 2

KINETIC PARAMETERS FOR 10^{-3}M SOLUTIONS OF Mn(III) IN DIFFERENT SOLVENTS

Solvent	Electrode	K°/cm.s^{-1}	∝
DMF	Ag	2.2×10^{-4}	0.30
	Au	4.2×10^{-4}	0.31
	G.C	8.1×10^{-4}	0.34
ACN	Ag	0.2×10^{-4}	0.29
	Au	0.8×10^{-4}	0.32
	G.C	1.2×10^{-4}	0.34
EtOH	Ag	0.1×10^{-5}	0.28
	Au	0.3×10^{-5}	0.35
	G.C	0.4×10^{-5}	0.32
MeOH	Ag	0.2×10^{-5}	0.31
	Au	0.3×10^{-5}	0.35
	G.C	0.5×10^{-5}	0.32

Analytical Validity

The good concentration plots in DMF and ACN encouraged an examination of the analytical application of RDE voltammetry. Examples of calibration results Tare given in Table 3. To appraise the reliability of rapid determination, a series of four solutions of manganese (III) standards was prepared and a single measurements of the limiting currents was made at each of five rotation speeds.

TABLE 3

EXAMPLE CALIBRATION RESULTS FOR THE DETERMINATION OF MANGANESE (III) ACETATE BY RED VOLTAMMETRY. RANGE: 0.7×10^{-3} mol 1^{-1}, ELECTRODE AREA (GLASSY CARBON), 0.28 cm^2; TEMPERATURE, 20°C, AND $n = 1$

Nominal rotation speed/rev. min^{-1}	Slope/ mA 1 mmol^{-1}	Intercept/ mA	Correlation Coefficient	*RSD of slope %
25	0.4231	0.0284	0.9982	2.42
50	-.5423	0.0146	0.9996	1.29
75	0.6212	0.0028	0.9995	1.92
100	0.7054	0.0037	0.9998	1.53
125	0.8527	0.0115	0.9996	1.25

*RSD = relative standard deviation.

The concentration was calculated from the slope and intercept and the percentage relative standard deviations for each concentration of five determinations are given in Table 4. Each results involves the propagation of errors from five calibrations, yet the mean relative standard deviation is just under 2.5%, less than 12 min being required for each set of measurements.

TABLE 4

PRECISION OF DETERMINATION BY RDE VOLTAMMETRY. EACH RESULT ARISES FROM THE MEASUREMENT OF LIMITING CURRENT AT EACH OF FIVE ROTATION SPEEDS

Manganese (III) acetate concentration		R.S.D. %		
Solvent	mmol l^{-1}	GC	Au	Ag
DMF	1.9985	2.41	2.31	2.42
	4.9886	2.12	1.92	2.32
	7.9675	1.85	1.92	1.67
	9.9328	1.52	1.42	1.28
ACN	1.9985	2.13	2.43	2.32
	4.9886	1.65	2.13	1.75
	7.9675	1.52	1.85	1.32
	9.9328	1.23	1.57	1.21

REFERENCES

1. E. Bishop (Ed.), Wilson and Wilson's Comprehensive Analytical Chemistry, Volume 2, Part D, Coulometric Analysis, Elsevier, Amsterdem and New York (1975).
2. D. R. Rosseinsky and R. J. Hill, *J. Chem. Soc., Faradny Trans. I*, **70**, 1140 (1974).
3. E. Bishop and P. Cofre, *Analyst*, **106**, 429 (1981).
4. R. Guidelli and G. Piccardi, *Electrochim. Acta*, **13**, 36 (1968).
5. G. Gritzner, K. Danksaqmuller and V. Gutmann, *J. Electroanal. Chem.*, **90**, 203 (1978).
6. V. Gutmann, G. Gritzner and K. Danksaqmuller, *Inorg. Chim. Acta*, **17**, 81 (1976).
7. G. Gritzner, K. Danksaqmuller and V. Gutmann, *J. Electroanal. Chem.*, **72**, 177 (1976).
8. G. Gritzner, *Inorg. Chim. Acta*, **24**, 5 (1974).
9. G. Gritzner, *Monatsh. Chem.*, **107**, 1055 (1976).
10. V. G. Levich, Physiochemical Hydrodynamics, Prentice Hall, Englewood Cliffs, NJ (1962).

11. U. Mayer, V. Gutmann and W. Gerger, *Monatsh. Chem.*, **106**, 1235 (1975).
12. F. A. Abeed, Ph.D. Thesis, University of Exeter, 1980.
13. F. A. Abeed, T. A. K. Al-Allaf and S. T. Sulaiman, *Analyst*, **113**, 333 (1988).
14. T. Beigler, E. R. Gonzalez and R. Parson, *Collect. Czech. Chem. Commun.*, **36**, 414 (1971).
15. W. Corski and Z. Galus, *J. Electroanal. Chem.*, **201**, 203 (1986).

[*Received*: 20 January 1989; *Accepted*: 15 March 1989] AJC—43