J. Indian Chem. Soc.,
Vol. LIX, July 1982, pp. 843-845

Studies on the Suppression of Polarographic Maximum of Mn(II) by Some uni- and poly-valent Cations vis-a-vis Their Influence on the Kinetics of the Electrode Reaction of Mn(II)

ASHOK KUMAR+, KAILASH CHANDRA and MUKHTAR SINGH

Department of Chemistry, Agra College, Agra-282 002

Manuscript received 13 July 1981, revised 17 March 1982, accepted 1 May 1982

Suppression of the polarographic maximum of Mn(II) in 0.05 *M* KCl, which falls in the category of the negative maximum of the first kind, has been attempted using some uni- and poly-valent metal cations, viz, Li^+, Na^+, K^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, La^{3+}, Nb^{3+} and Pr^{3+} as suppressors. The electrode reaction of Mn(II) has been found to be quasi-reversible in the presence of different amounts of these suppressors. The values of kinetic parameters (α and $k_{s,h}$) of quasi-reversible electrode reaction of Mn(II) have been calculated by Gellings' method. A decrease in the values of α and $k_{s,h}$ with increasing concentrations of uni- and poly-valent cations shows that the quasi-reversible electrode reaction of Mn(II) tends towards irreversibility. On the basis of molarity, the order of relative efficacies of metal cations in the suppression of the negative maximum of Mn(II) has been established as $M^{3+} > M^{2+} > M^+$.

LAL and Srivastava[1-2] reported that Mn(II) exhibited a negative maximum of first kind in KCl and attempted its suppression by some aliphatic alcohols and also by various cations. They reported that in the presence of Th^{4+} ions, the maximum of Mn(II) is more exalted than suppressed. This observation contradicts the statement[3] that heavy metal cations suppress the maxima more readily than do those of light elements. The central idea of these studies has been to find the optimum concentration at which the maximum is just suppressed and then to formulate an order of efficacies on the molarity scale. Recently, Ram *et al*[4] have attempted the suppression of the maximum of Mn(II) by various ionic (both cationic and anionic) and non-ionic surfactants and compared their relative efficacies in the suppression of this maximum on the basis of their characteristic properties. In the present paper an attempt has been made to suppress the maximum of Mn(II) by some uni- and poly-valent cations and then to study the influence of these cations on the kinetics of the electrode reaction of Mn(II). The order of relative efficacies of uni- and poly-valent cations in the suppression of the maximum of Mn(II) has been established on the basis of molarity scale of concentration.

Experimental

All the chemicals used were of reagent grade and their stock solutions were prepared in conductivity water. The concentration of Mn(II) (using $MnCl_2 \cdot 2H_2O$) was kept at 1.0×10^{-3} *M* in each case. 0.05 *M* KCl was used as the supporting electrolyte. The polarograms of the solutions were taken on a manual set-up[5]. Stock solutions (2 *M*) of Li, Na, K (as nitrates) and of Ba, Sr, Ca and Mg (0·1 *M*) (as nitrates) were prepared by direct weighing from A.R., B.D.H., samples. The concentrations of the rare earth cations (as nitrates) in their stock solutions were determined by standard methods[6-7]. Solutions of desired molarity were prepared from these stock solutions of known concentrations by dilution.

The experimental conditions such as the concentration of the depolarizer, the concentration of the supporting electrolyte (KCl), *p*H and the height of mercury column were adjusted in such a way as to obtain a sharp and well-defined maximum of Mn(II). These conditions were kept the same in all the cases throughout the study. Thus, the concentration of the depolarizer was kept at 1.0×10^{-3} *M*, that of the supporting electrolyte at 0.05 *M*, the *p*H of the medium at 6.0 (by adding very dilute solutions of HCl or NaOH) and the height of the mercury column (h_{corr}) at 71.45 cm.

Results and Discussion

The first kind polarographic maximum of Mn(II) under the chosen experimental conditions appears at -1.53V (vs S.C.E.). This lies well on the negative side of the electro-capillary curve and hence the maximum of Mn(II) is of negative polarity[8]. Representative Fig. 1 depicts the morphology of

+ Department of Chemistry, St. John's College, Agra.

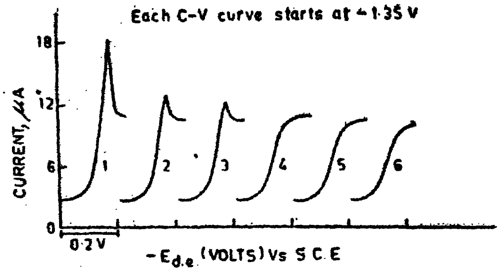

Fig. 1. C-V curves of Mn(II) in the presence of increasing concentrations of Mg^{2+}.
1. 0.0 *M*, 2. 0.7×10^{-3} *M*, 3. 1.1×10^{-3} *M*, 4. 1.2×10^{-3} *M*, 5. 2.8×10^{-3} *M*, 6. 4.0×10^{-3} *M*.

C-V curves of Mn(II) in the presence of increasing concentrations of Mg^{2+}.

E_{max} of Mn(II) gets shifted to positive potentials (Table 1) with increasing concentrations of uni- and poly-valent cations. The value of i_{max} decreases sharply before the suppression of the maximum, which indicates that the negative maximum of Mn(II) is susceptible to suppression by the requisite amounts of uni- and poly-valent cations. After the suppression of the maximum, Mn(II) yields, in each case, a well-defined wave which is diffusion-controlled.

TABLE 1—POLAROGRAPHIC CHARACTERISTICS AND KINETIC PARAMETERS FOR THE ELECTRODE REACTION OF Mn(II) IN THE PRESENCE OF INCREASING CONCENTRATIONS OF UNI- AND POLY-VALENT CATIONS AT 25±0.1°. h_{corr} = 71.45 cm ; t = 3.1 sec ; m = 2.2 mg/sec ; $m^{2/3}t^{1/6}$ = 2.03 $mg^{2/3}$ $sec^{-1/2}$ (IN 0.05 *M* KCl, OPEN CIRCUIT).

[Cation] *M*	$-E_{max}$ (S. C. E.)	$-E_{1/2}$ (S. C. E.)	i_{max} μA	i_d μA	Slope mV	D × 10^6 cm^2/sec	α	$k_{s,h}$ (× 10^3) cm/sec
0.0	1.53	–	15.71	–	–	–	–	–
× 10^1				Li^+				
0.8	1.52	–	14.73	–	–	–	–	–
1.6	1.51	–	8.90	–	–	–	–	–
2.0*	No max	1.489	–	7.51	41	6.85	0.80	8.62
11.6	,,	1.493	–	5.70	47	3.95	0.75	5.13
				Na^+				
0.6	1.52	–	14.32	–	–	–	–	–
0.7	1.51	–	7.78	–	–	–	–	–
0.8*	No max	1.489	–	7.64	40	7.11	0.80	7.22
3.2	,,	1.492	–	5.84	44	4.15	0.72	1.55
				K^+				
0.5	1.52	–	12.51	–	–	–	–	–
1.1	1.51	–	7.92	–	–	–	–	–
1.3*	No max	1.495	–	7.41	41	6.85	0.81	6.10
4.8	,,	1.500	–	6.25	45	4.76	0.75	3.14
× 10^3				Ba^{2+}				
0.2	1.52	–	10.15	–	–	–	–	–
0.3	1.51	–	8.76	–	–	–	–	–
0.4*	No max	1.497	–	7.64	40	7.11	0.84	2.80
5.4	,,	1.500	–	6.39	43	4.97	0.74	2.06
				Sr^{2+}				
0.1	1.52	–	11.26	–	–	–	–	–
0.4	1.51	–	7.92	–	–	–	–	–
0.5*	No max	1.490	–	7.51	40	6.85	0.85	4.08
5.5	,,	1.500	–	6.81	44	5.64	0.68	2.63
				Ca^{2+}				
0.1	1.52	–	10.29	–	–	–	–	–
0.5	1.51	–	8.34	–	–	–	–	–
0.8*	No max	1.480	–	7.23	39	6.36	0.85	8.24
2.3	,,	1.483	–	6.12	42	4.55	0.80	4.41
				Mg^{2+}				
0.7	1.52	–	10.01	–	–	–	–	–
1.1	1.51	–	9.17	–	–	–	–	–
1.2*	No max	1.490	–	7.78	40	7.37	0.83	6.30
4.0	,,	1.493	–	7.23	43	6.36	0.75	5.49
× 10^6				La^{3+}				
0.2	1.53	–	13.48	–	–	–	–	–
0.7	1.52	–	12.10	–	–	–	–	–
1.0	1.52	–	8.48	–	–	–	–	–
1.2*	No max	1.490	–	7.37	40	6.60	0.86	5.20
1.5	,,	1.495	–	6.95	42	5.88	0.75	3.89
				Nb^{3+}				
0.2	1.52	–	13.62	–	–	–	–	–
0.7	1.51	–	9.87	–	–	–	–	–
1.0*	No max	1.490	–	7.51	40	6.85	0.87	5.29
1.5	,,	1.495	–	6.67	42	5.41	0.77	4.89
				Pr^{3+}				
0.6	1.52	–	10.29	–	–	–	–	–
0.9	1.51	–	7.92	–	–	–	–	–
1.0*	No max	1.493	–	6.95	41	5.88	0.88	8.56
2.0	,,	1.495	–	6.81	43	5.64	0.78	6.49

* Concentration at which the maximum just disappears.

A perusal of slope values (Table 1) of log plots shows that the slope values of 2-electron reduction process of Mn(II) lie in the range 39-49 mV which indicates[9-13] that the polarographic reduction of Mn(II) is quasi-reversible in the presence of increasing amounts of uni- and poly-valent cations. The values of kinetic parameters (α and $k_{s,h}$) of the quasi-reversible electrode reaction of Mn(II) have been calculated by Gellings' method[14]. The values of $k_{s,h}$ are of the magnitude of 10^{-3} cm/sec which confirm[15,16] the quasi-reversible nature of the electrode reaction of Mn(II). It is observed that the value of $k_{s,h}$ decreases with increasing concentrations of uni- and poly-valent cations. This shows that the quasi-reversible electrode reaction of Mn(II) tends towards irreversibility with increasing concentrations of uni- and poly-valent cations. It is also evident from Table 1 that the value of α decreases with increasing concentrations of the cations thereby showing that the quasi-reversible electrode reaction of Mn(II) tends towards irreversibility. The variations in the values of $k_{s,h}$ and α thus lead to the same conclusion. Further, a negative shift in $E_{1/2}$ and a decrease in i_d with increasing concentrations of uni- and poly-valent cations lend support to the conclusion arrived at on the basis of the variations in the values of $k_{s,h}$ and α.

By comparing the concentrations (on the molarity scale) of the various uni- and poly-valent cations at the stage where the maximum gets just suppressed, the order for the relative efficacies of various uni- and poly-valent metal cations in the suppression of negative maximum of Mn(II) has been established as $M^{3+} > M^{2+} > M^{+}$.

Acknowledgement

Financial assistance to one of the authors (A. K.) from U. G. C., New Delhi is gratefully acknowledged.

References

1. S. LAL and S. N. SRIVASTAVA, *Indian J. Chem.*, 1968, **6**, 382.
2. S. LAL and S. N. SRIVASTAVA, *Indian J. Appl. Chem.*, 1969, **32**, 287.
3. J. HEYROVSKY and J. KUTA, "Principles of Polarography", Academic Press, New York, 1966, p. 438.
4. G. RAM, M. C. DUBEY and M. SINGH, *Indian J. Chem.*, 1979, **17A**, 452.
5. S. K. JHA, ASHOK KUMAR, (KM.) ANJU VARSHNEY, (KM.) KRISHNA and M. SINGH, *J. Indian Chem. Soc.*, 1979, **56**, 1259.
6. I. M. KOLTHOFF and R. ELMQUIST, *J. Amer. Chem. Soc.*, 1931, **53**, 1225, 1235.
7. G. SCHWARZENBACH, "Complexometric Titrations", Methuen & Co. Ltd., New York, 1969, p. 73.
8. J. HEYROVSKY and J. KUTA, "Principles of Polarography", Academic Press, New York, 1966, p. 437.
9. J. N. GAUR, D. S. JAIN and A. KUMAR, *Indian J. Chem.*, 1975, **13**, 165.
10. P. S. VERMA, D. S. JAIN and J. N. GAUR, *Indian J. Chem.*, 1975, **13**, 586.
11. S. S. SHARMA, S. K. JHA and M. SINGH, *Z. Naturforch.*, 1977, **32B**, 416.
12. S. S. SHARMA, S. K. JHA and M. SINGH, *Indian J. Chem.*, 1977, **15A**, 923.
13. S. S. SHARMA and M. SINGH, *J. Indian Chem. Soc.*, 1980, **57** 21.
14. P. J. GELLINGS, *Z. Elektrochem. Ber. Bunsenges, Phys. Chem.*, 1962, **66**, 477, 481, 799 ; 1963, **67**, 167.
15. P. DELAHAY, *J. Amer. Chem. Soc.*, 1953, **75**, 1430.
16. H. MATSUDA and Y. AYABE, *Z. Elektrochem.*, 1959, **63**, 1164.