

Kinetics of hydrogen evolution reaction on bright platinum electrode in aqueous dimethylformamide solutions by cyclic voltammetry

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Kinetic behaviour of hydrogen evolution reaction (HER) has been studied on bright platinum electrode in aqueous mixtures of 0, 25, 50, 75, 90 and 100 wt% N,N-dimethylformamide (DMF) from both HCl and HClO₄ solutions by cyclic voltammetry under varying sweep rates [500-1 mVs⁻¹] in the cathodic potential region of 0-1000 mV. The cyclic voltammograms are characterized by single cathodic and the corresponding anodic peaks and are found to be quasi-reversible in nature. The relevant kinetic parameters like the diffusion coefficient (D_R) of the reductant and the rate constant (k_s) (based on apparent area of the electrode) have been derived using the formulations of Shain and Nicholson. The values of D_R and k_s in aq. DMF mixtures decrease from that in pure water due to possible increased protophilicity of DMF-water mixtures which hinders the solvated H⁺ ions to approach the electrode surface for undergoing HER.

As a part of our studies on electrocatalytic behaviour of different electrodes with a view to developing a desirable reversible hydrogen electrode (RHE) suitable in some aquo-organic solvents, in a previous paper¹ we have reported the kinetics of hydrogen evolution reaction (HER) on a bright platinum (Pt) electrode in aqueous mixtures of ACN from both HCl and HClO₄ solutions using cyclic voltammetry. With a view to examining the feasibility of RHE in aqueous DMF mixtures similar studies have now been extended to the aq.DMF mixtures of different compositions with HCl and HClO₄ (~ 0.001 mol dm⁻³) serving as the electrolytes and 0.1 mol dm⁻³ NaClO₄ as the supporting electrolyte. The kinetic parameters have been evaluated employing Nicholson's formulations² applicable to the quasi-reversible systems as observed in the present study. The observed kinetic parameters have been interpreted in terms of the relative difficulties of diffusion of solvated H⁺ species from bulk to the electrode surface and the subsequent fast charge transfer across the interface forming adsorbed H atoms followed by desorption of the formed hydrogen molecules in the gaseous state.

Materials and Methods

Dimethylformamide (DMF; AR, SD) was dried over neutral aluminium oxide (Sisco Res. Lab., India) for a few days followed by fractional distillation under reduced pressure, collecting the middle fractions only. Hydrochloric acid and HClO₄ (both E. Merck) were used for preparing electrolyte solutions.

The supporting electrolyte NaClO₄ (E. Merck) was dried *in vacuo*.

The working acid solutions (conc. range 1 to 8 × 10⁻³ mol dm⁻³) containing NaClO₄ (0.1 mol dm⁻³) were prepared in aq.DMF mixtures containing 0, 25, 50, 75, 90 weight %DMF. In pure DMF however tetraethylammonium perchlorate (GFS Chemicals, USA) was used as the supporting electrolyte. Water content resulting from 1 to 8 × 10⁻³ mol dm⁻³ HCl or HClO₄ solution was taken to be negligibly small. Working solutions were purged with pure N₂ gas presaturated with the respective solvent for about 20 min to remove dissolved oxygen. The cell used was of conventional type³ with three-electrode assembly in one compartment. A bright Pt-foil [4 cm² geometric area (A)] and a bright Pt-wire (A=0.2 cm²), both pretreated by usual procedures⁴, were used as the counter electrode and the working electrode respectively. The reference electrode employed was a doubly jacketed aqueous saturated calomel electrode³, SCE(w) (Fischer, E 6 A).

Measurements were made employing a set up consisting of a Standard Potentiostat (Wenking, model VSG 72) and a Houston Omnigraphic (model 2000) x-y recorder. The potential range employed was from 0 to -1 V and the voltage sweep rates (v) used were in the range of 0.5 to 0.002 Vs⁻¹.

In view of the fact that the products of the cathodic reduction of H⁺ ions are M-H and thence H₂ molecules, and some of which are likely to get desorbed, the constancy of E_p as well as $i_{p,c}/i_{p,a}$ values

Table 1—Cyclic voltammetric parameters, E_p (mV) and i_p (mA cm^{-2}) of HER on bright Pt under different scan rates and the evolved D ($\text{cm}^2 \text{s}^{-1}$) of H_3O^+ and the rate constant k_s (cm s^{-1}) in some aqueous mixtures of DMF at 25°C

Scan rate (Vs^{-1})	Para- meter	DMF (wt%)													
		Water		25		50		75		90		95	99	Pure	DMF
		HCl 3.71 mM	HClO_4 3.58 mM	HCl 2.46 mM	HClO_4 6.58 mM	HCl 2.33 mM	HClO_4 6.35 mM	HCl 3.23 mM	HClO_4 7.70 mM	HCl 5.52 mM	HClO_4 5.87 mM	HCl 5.89 mM	HClO_4 6.18 mM	HCl 5.94 mM	HClO_4 6.65 mM
0.5	$-E_p$	495	495			550			525			540			
	i_p	5.21	5.02			1.24			2.61			1.14			
0.4	$-E_p$	485								525	460	522		570	
	i_p	4.96								0.89	0.88	1.0		1.76	
0.3	$-E_p$	480	485	515	575	520	625	590	510	515	450	513	450	555	440
	i_p	4.54	4.31	1.65	3.17	1.07	1.79	0.85	2.10	0.85	0.74	0.88	1.37	1.61	1.79
0.2	$-E_p$	475	480	505	565	510	615	570	505	500	440	508	440	530	435
	i_p	4.04	3.61	1.40	2.61	0.87	1.46	0.71	1.80	0.72	0.57	0.72	1.12	1.18	1.49
0.1	$-E_p$		470	500	550	500	605	550	495	485	430	494	435	510	430
	i_p		2.96	1.01	2.02	0.62	1.07	0.53	1.26	0.55	0.38	0.54	0.81	0.99	0.98
0.05	$-E_p$	460	470	500	545	495	600	525	485	470	425	476	430	485	425
	i_p	2.33	2.54	0.74	1.51	0.43	0.79	0.36	0.92	0.38	0.31	0.39	0.62	0.71	0.67
0.03	$-E_p$	455	465	500	545	495		515	485	465	410	471	425	475	420
	i_p	1.91	2.09	0.56	1.21	0.36		0.28	0.75	0.29	0.29	0.30	0.56	0.60	0.65
0.02	$-E_p$	455	465	500	545	495	600	505	485	460	410	462	420	460	420
	i_p	1.68	1.99	0.48	1.03	0.29	0.62	0.22	0.62	0.23	0.28	0.24	0.45	0.47	0.52
0.01	$-E_p$	455	460	500	545		600	490	485	450		448	420	450	420
	i_p	1.32	1.40	0.38	0.82		0.49	0.15	0.44	0.15		0.16	0.33	0.33	0.40
0.005	$-E_p$		460					480	485	450		425	420	440	420
	i_p		1.12					0.09	0.38	0.10		0.13	0.24	0.26	0.36
0.003	$-E_p$		460					480				405			
	i_p		1.01					0.06				0.1			
0.002	$-E_p$		460					480				405		440	
	i_p		0.91					0.04				0.08		0.20	
	$D_{\text{H}^+} \times 10^6$	23.9	32.8	3.1	2.1	1.2	0.7	0.1	0.4	0.2	0.2	0.2	0.3	0.6	0.4
	$k_s \times 10^3$	5.3	9.3	4.8	3.1	2.5	1.8	0.4	1.4	0.3	0.6	0.2	0.8	0.5	0.9

with scan rates was not maintained in these cases. But the approximate constancy of $E_{p,c}$ values at the lower scan rates especially below $20\text{--}10 \text{ mVs}^{-1}$ could be taken as examples of quasi-reversible character in all the compositions.

Results

Figure 1 represents some typical cyclic voltammograms (CVGs) at different scan rates for the electrochemical process: $\text{H}_{\text{solv}}^+ + e^- (\text{M}) = (1/2)\text{H}_2(\text{g})$ as observed on $\text{M} = \text{bright Pt}$ surface in different DMF-water mixtures. The CVGs are characterized by single cathodic peak with peak potential $E_{p,c}$ and the corresponding anodic peak with peak potential $E_{p,a}$ in all the solvents in the potential range of 0 to -1000 mV indicating that HER follows an identical mechanism in each case. Table 1 presents the

cyclic voltammetric parameters like $E_{p,c}$ and the corresponding cathodic peak currents $i_{p,c}$ at different scan rates in different DMF-water mixtures. The constancy of $E_{p,c}$ with scan rates at low sweep rates $< 20 \text{ mVs}^{-1}$ and their reasonable variation at higher scan rates are indicative of the quasi-reversible nature of CVGs in all aq.DMF mixtures.

At low sweep rates where reversibility persists, the values of diffusion coefficients (D_R) of the reductant (H^+)_{solv} were derived from the slopes of the linear plots of $i_{p,c}$ versus $v^{1/2}$ as expected from Shain and Nicholson's expression^{1,2}, for reversible peak ($i_{p,c}$)_{rev} on the apparent area (see Eq. 1).

$$(i_{p,c})_{\text{rev}} = 0.269 n^{3/2} C_R D_R^{1/2} v^{1/2} \quad \dots (1)$$

In Eq. 1 the various terms have their usual significance. Typical i_p versus $v^{1/2}$ plots for HER in differ-

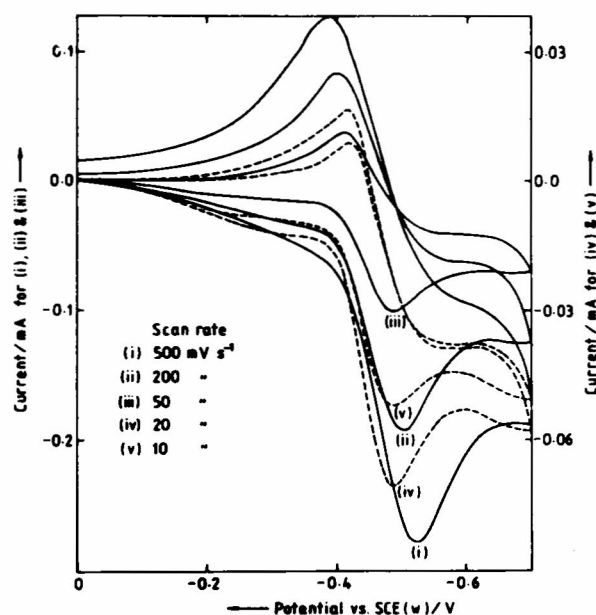


Fig. 1—Typical cyclic voltammograms at different scan rates of HER with HClO_4 solution in 75 wt% DMF on a bright platinum electrode at 25°C

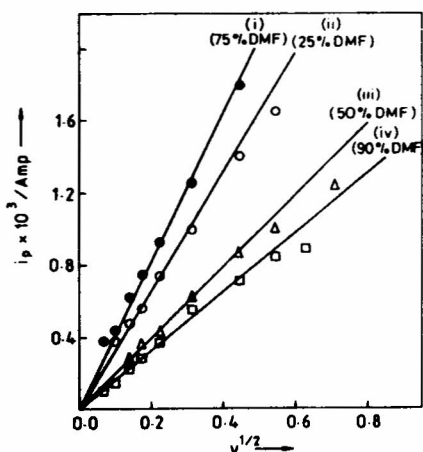


Fig. 2—Some typical i_p versus $v^{1/2}$ plots for HER in aqueous DMF mixtures for HClO_4 (i) and HCl [(ii), (iii) and (iv)] at 25°C

ent aq. DMF mixtures are presented in Fig. 2 and D_R values are presented in Table 1.

The values of rate constant (k_s) of the reaction on the unit apparent area of Pt surface were obtained, as before¹, using Shain and Nicholson's expression² for the reversible and irreversible peak potentials

$$(E_{p,c})_{\text{rev}} = E_{1/2} - 1.1RT/nF \quad \dots (2)$$

$$(E_{p,c})_{\text{irrev}} = E_{1/2} - b[0.52 - (1/2)\log b/D_R - \log k_s] - (b/2)\log v \quad \dots (3)$$

where $E_{1/2}$ is the half-wave potential of redox reaction and b is the Tafel slope being equal to $RT/\alpha nF$

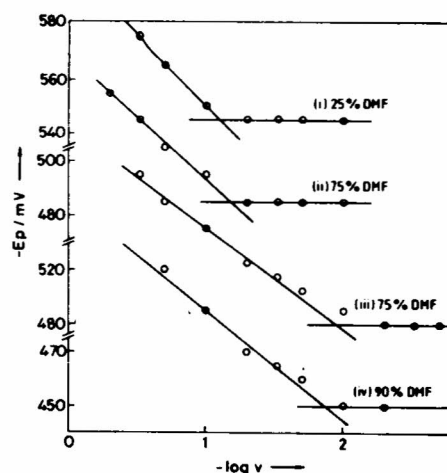


Fig. 3—Some typical $-E_p$ vs $-\log v$ plots for HER on bright Pt in aqueous DMF mixtures for HClO_4 [(i) and (ii)] and HCl [(iii) and (iv)] at 25°C

where α is the transfer coefficient. Some typical plots of E_p vs $\log v$ are presented in Fig. 3. The values of b were obtained from the slopes of the observed linear plots in Fig. 3 in the irreversible region. The desired values of rate constant k_s were evaluated as before¹ by combining Eqs (2) and (3) at sweep rate $v = v_c$ where transformation from reversible behaviour to the irreversible one occurred, i.e. from the point of intersection of the plots of $E_{p,c}$ versus $\log v$ in reversible and irreversible region so that

$$E_{1/2} - 1.1RT/nF = E_{1/2} - b[0.52 - (1/2)\log(b/D_R) - \log(k_s)] - (b/2)\log v_c \quad \dots (4)$$

The k_s values were therefore obtained using Eq. (5)

$$\log(k_s) = 0.52 - (1/2)\log(b/D_R) + (1/2)\log v_c - 1.1RT/bnF \quad \dots (5)$$

The values of k_s so obtained are presented in Table 1.

Discussion

From Table 1 it appears that D_R values in various aq. DMF mixtures decrease by about an order as compared with that in water, which is found to be more or less in agreement with the literature value⁵. The profiles of D_R as well as k_s versus solvent composition are compared with those of ACN-water mixtures reported earlier¹ in Fig. 4. It appears that while D_R values in DMF-water mixtures decrease sharply at low percentage of DMF, it levels off at higher content of DMF. The same in ACN-water mixtures however decrease more or less monotonically. Seemingly, the diffusion of H_{solv}^+ in aqueous DMF mixtures is hindered by the possible formation of large sized solvated H^+ , i.e. $(\text{H}_{\text{solv}}^+)$, due to

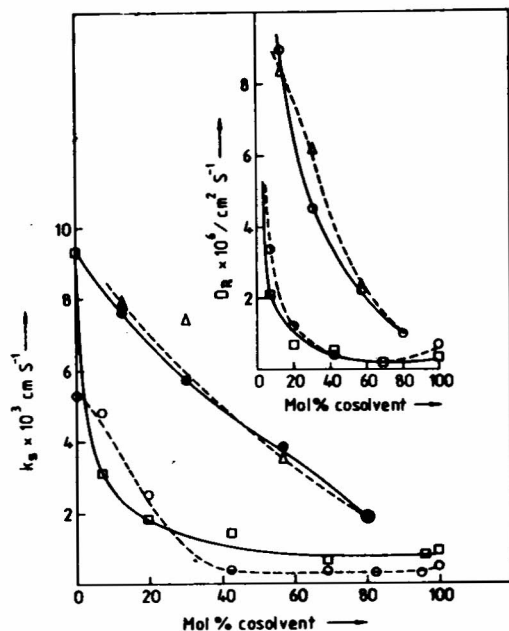
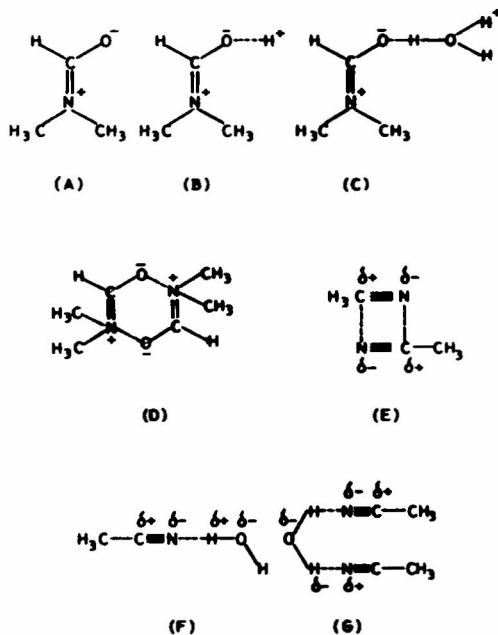


Fig. 4—Variation of k_s and D_R (inset) values with composition for HER in aqueous mixtures of DMF [○ HCl and □ HClO_4] and ACN [△ HCl and ⊕ HClO_4] at 25°C

larger protophilicity⁶ of DMF molecules having the possible zwitterionic form (A) which helps formation of the hydrates^{7,8} either (B) or (C) in its aqueous mixtures. The increased basicity of aqueous DMF mixtures is also evident from the observed negative magnitudes of transfer free energies of H^+ , $\Delta G_i^0(\text{H}^+)^{9,10}$. The observed levelling off of D_R -composition profiles in aq.DMF mixtures having higher DMF percentage is seemingly due to the superimposed effects of the gradual desolvation of $(\text{H}^+)_{\text{solv}}$ because of increased aproticity of the solvents which arises from the possible formation of $(\text{DMF})_2$ clusters (D). This is evident not only from the upward trend of $\Delta G_i^0(i)$ -composition profile of H^+ (refs 9, 10) but also from the sharp rise of $\Delta G_i^0(i)$ of the anions like Cl^- , Br^- , I^- (ref. 10) and OH^- (ref. 11).

In the case of ACN-water mixtures, despite intrinsic protophobicity of ACN molecules because of the possible formation of $(\text{ACN})_2$ dimers like (E), the possible formation of H-bonded ACN- H_2O (F) and $(\text{ACN})_2$ - H_2O (G) complexes in its aqueous mixtures, H^+ is likely to be solvated by the O centres with negative formal charges of the complexes (F) and (G) which are seemingly responsible for the observed monotonic decrement of D_R values with increase in the proportion of ACN in aq.AC. The effect of aproticity due to the $(\text{ACN})_2$ aggregates (E) on D_R values does not however seem to be that significant as in the case of DMF-water mixtures. The values of



rate constant (k_s) in Table 1 and the k_s -composition profiles in Fig. 4 also suggest that these are having more or less similar trends as that of D_R values in the respective solvent systems. The rate of HER which is fairly facile in pure H_2O , becomes increasingly sluggish with increase in the proportions of both the cosolvents. As is expected for quasi-reversible reactions, this behaviour of k_s may be attributed partly to the behaviour of D_R and subsequent quantum tunnelling¹² of the reductant (H^+) and partly to the effectively free uncovered fraction $(1 - \theta_s)$ of the Pt electrode, where θ_s is the fraction of the surface covered by the solvent molecules, besides the intrinsic catalytic activity of Pt. Since the polarisability (α_s) and dipole moment (μ_s) of the solvent molecules are likely to guide θ_s (ref. 13) values and their values for the three solvent molecules H_2O , ACN and DMF are 1.44, 4.41 and 7.90 Å³ (ref. 13) and 1.86, 3.44, 3.86 D (ref. 14) respectively, it is expected that θ_s values will have the order $\text{H}_2\text{O} > \text{ACN} > \text{DMF}$.

Since the intrinsic catalytic activity of the common Pt electrode surface is independent of solvent, it remains the same in all the solvents. Also, the solvated radii of the reductant $(\text{H}^+)_{\text{solv}}$ dictating the diffusion coefficient and the capability of quantum tunnelling for the charge transfer reaction across the interface in these solvents are of the same order. So, it appears that the rate constant k_s for HER in the aqueous DMF and ACN mixtures are in accord with what is expected from the relative solvation of the reductant $(\text{H}^+)_{\text{solv}}$ as well as the relative $(1 - \theta_s)$ values in these solvents. The difference in D_R or k_s values resulting from HCl and HClO_4 solutions in

each of the cosolvent may be taken to be fairly small and hence seemingly insignificant. The apparent differences in k_s values in aqueous DMF may possibly be due to the effect of larger specific adsorption of Cl^- as compared to that of ClO_4^- , if any, in these aquo-organic solvent systems as in pure water¹².

Thus the present results show that as in the case of aqueous mixtures of ACN, the electrocatalytic activity of bright Pt decreases in aqueous DMF mixtures also and it cannot be used as RHE in pure DMF as well as in its aqueous mixtures.

Acknowledgement

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