

Thermodynamic and kinetic behavior of hydrogen electrode in a solution of 0.5 M KClO₄ in dimethyl sulphoxide

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(Received 22 August 2002, revised 3 March 2003)

Abstract: The hydrogen electrode on an interface platinum/dimethyl sulphoxide + 0.5 M KClO₄ solution was examined from both the thermodynamic and kinetic aspect, using HCl as a proton source. The equilibrium potential was shown to obey a Nernstian dependence on concentration. The voltammograms recorded using a rotating platinum disc electrode evidenced that the cathodic evolution of hydrogen proceeds under mixed, activation–diffusion control. The diffusion coefficient of the proton was determined to amount to $4.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. In the region of activation control, a Tafel slope of about 0.110 V dec^{-1} was estimated, which indicates that the Volmer reaction is the rate determining step.

Keywords: dimethyl sulphoxide, equilibrium potential, hydrogen electrode, hydrogen evolution, rotating disc.

INTRODUCTION

Nowadays, aprotic electrolytic solutions are attracting increasing attention owing to their wide application in modern electrochemical devices, such as lithium batteries and electrolytic capacitors.^{1–4} Dimethylsulphoxide (DMSO) belongs to the group of mostly used aprotic solvents. The electrochemical behavior of many redox couples in this solvent⁵ as well as its own electrochemical behavior have been reviewed.^{5,6}

The conductivities of HCl – DMSO solutions were measured earlier,^{7–9} and these investigations evidenced that the conductivity is substantially lower in this aprotic solvent than in aqueous solutions, probably as a consequence of the fact that the proton does not display abnormal mobility. Also, the pronounced curvature in the plot of molar conductance *versus* the square root of concentration indicates a substantial role of ionic associations. The limiting molar conductivity of the H⁺ ion may be calculated from the limiting molar conductivity of HCl ($38.74 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$),⁹ after subtraction of the contribution of the Cl[–] ion ($24.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$),¹⁰ to amount to $14.74 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

Recently, the electrochemical behavior of acids on platinum electrodes in organic solutions were examined primarily from an electroanalytical standpoint. Barrette *et al.*,¹¹ us-

ing linear sweep voltammetry, investigated the relative acidity of various Brønsted acids in DMSO and in other aprotic solvents, on the basis of the relative positions of the half-wave potentials of the hydrogen electrode. They found that the half-wave potential for hydrogen evolution from a $\text{HClO}_4 + \text{DMSO} + 0.5 \text{ M}$ tetraethylammonium perchlorate solution on a smooth platinum electrode amounts to -0.218 V vs. SHE (-0.459 V vs. SCE). A similar study involving DMSO, in which particular attention was paid to the mechanism of the reduction of acids, was performed by Treimer *et al.*¹² They also calculated the formal potential of the hydrogen electrode in acid + DMSO solutions in dependence of $\text{p}K$, using the data¹⁷ that the solubility of hydrogen in DMSO at 25°C at 101.3 kPa (1 atm) amounts to 1.07 mM . They showed that the formal potential does not depend on the equilibrium constant (K_{d}) of acid dissociation for strong acids having $\text{p}K$ values less than 2.

Using cyclic voltammetry to determine the half-wave potential of hydrogen evolution from HClO_4 in various aprotic solvents, Daniele *et al.*^{13,14} studied both the relative solvents basicity¹³ and the proton-solvent interactions.¹⁴ On finding that the anodic-to-cathodic peak potential difference increases with the increase in sweep rate,¹³ they suggested that the hydrogen reduction is not completely reversible.

The diffusion coefficient of H^+ ion in $\text{HCl} + \text{DMSO} + 0.1 \text{ M}$ tetraethylammonium perchlorate was determined by the amperometric titration technique¹⁵ to amount to 4.29×10^{-6} . This value is close to the one reported previously by Kolthof *et al.*,¹⁶ who found polarographically using DME in the solution 8.9 mM HClO_4 in $\text{DMSO} + 0.1 \text{ M NaClO}_4$, that the H^+ diffusion coefficient amounts to $4.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 30°C . Treimer *et al.*¹² using chronocoulometry found that the diffusion coefficient of H^+ in $1.39 - 2.03 \text{ mM}$ 4-methylbenzenesulfonic acid in $\text{DMSO} + 0.2 \text{ M}$ tetraethylammonium perchlorate amounts to $(2.76 \pm 0.06) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

This detailed survey of both old and recent literature shows that, although there exists the possibility to conclude that hydrogen evolution on platinum from DMSO solutions is approximately reversible,¹¹⁻¹⁴ no study aimed particularly at the thermodynamics and kinetics of the hydrogen redox processes in DMSO exists, unlike the case of aqueous media. In this work the concentration dependence of both the equilibrium potential on platinized platinum and the exchange current density on smooth platinum rotating disc, using hydrogen chloride as the proton source, were examined. Potassium perchlorate as an inert electrolyte was used, since it is soluble enough in DMSO, not-hygroscopic and electrochemically inert over a wide potential range. It may, therefore, be recommended as a standard inert electrolyte in this type of solvent.

EXPERIMENTAL

Dimethyl sulphoxide, Koch-Light Lab. Ltd, spectroscopic grade, in which dry KClO_4 was dissolved in the concentration of 0.5 M , was exposed to a stream of dry gaseous hydrogen chloride. In order to determine the concentration of the dissolved HCl , a sample of the solution was added to an excess of water and titrated using a standard NaOH solution. The initial HCl solution, the concentration of which was 0.0468 M , was diluted by addition of the supporting solution $\text{DMSO} + 0.5 \text{ M KClO}_4$ in order to obtain a series of solutions of lower concentrations. For comparison, a 0.01 M HClO_3 solution was also prepared by dissolving concentrated $60\% \text{ HClO}_3$ in the $\text{DMSO} + 0.5 \text{ M KClO}_4$ solution.

The viscosities of the solutions were measured using a Ostwald capillary viscometer.

All the electrochemical measurements were carried out using a EG&G PAR Model 270 Potentiostat/Galvanostat, equipped with an EG&G PAR 5208 Two Phase Lock-in Analyzer for impedance measurements. The electrochemical cell was thermostated at 25 °C. A commercial aqueous saturated calomel electrode was used as the reference electrode. For potential measurements, a platinized platinum foil was exposed to a gaseous hydrogen stream until a stationary potential value was attained. For electrode kinetics measurements, a smooth polycrystalline platinum disc electrode was prepared by polishing with α -Al₂O₃ polishing powders of gradually decreasing granulation, to obtain a mirror reflectance. During the kinetic experiments, the solutions were kept under an argon atmosphere. The elimination of oxygen was necessary since, for a supporting electrolyte solution equilibrated with air, the limiting current density of oxygen reduction on a rotating Pt disc at a rotation rate of 5 rps amounts to 0.62 mA cm⁻². To calculate the IR correction, the electrolyte resistance in the electrochemical cell was measured by the complex impedance method.

RESULTS AND DISCUSSION

The equilibrium potential plotted against the logarithm of HCl concentration, at atmospheric hydrogen pressure, presents a straight line with a slope of 0.060 V per decade (Fig. 1). This value confirms the expectation that, according to the first derivation of Nernst equation:

$$\frac{dE}{d \log c_{\text{H}^+}} = \frac{2.303 RT}{F} = 0.059 \text{ V} \quad (1)$$

the reaction $\text{H}^+ + e^- = 1/2 \text{H}_2$ determines the equilibrium potential. The extrapolation of this line to the zero of the $\log c$ axis gives -0.345 V vs. aqueous SCE to be the formal potential of the hydrogen electrode in the solution DMSO + 0.5 M KClO₄. A rather fair linearity of E vs. $\log c$ indicates that the KClO₄ supporting electrolyte enables the activity coefficients to main-

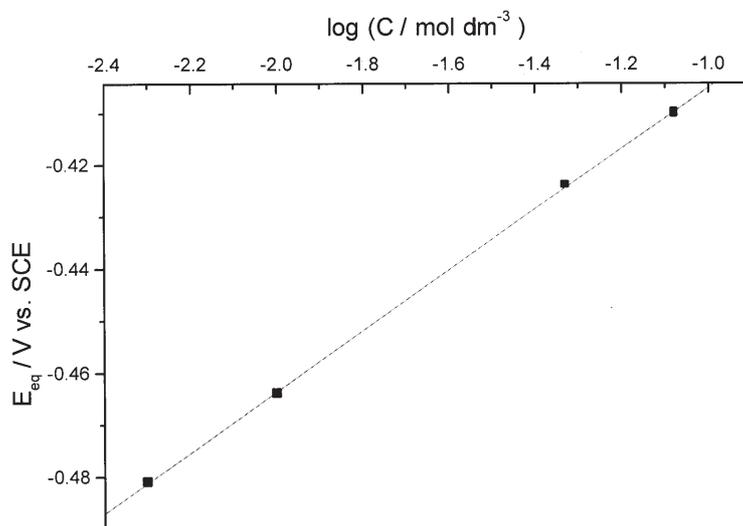


Fig. 1. Equilibrium potential of the hydrogen electrode on the boundary platinized platinum / DMSO + 0.5 M KClO₄, at 25 °C versus logarithm of concentration.

tain a fixed value over a large HCl concentration range $0.08\text{--}0.005\text{ mol cm}^{-3}$, contrary to the unsupported HCl + DMSO solution, the conductivity of which indicates a permanent decrease of activity coefficient with increasing HCl concentration.⁷⁻⁹

Examples of the current-potential curves obtained using the platinum rotating disc electrode in the solution DMSO + 0.5 M KClO₄ + 0.01 M HCl are shown in Fig. 2.

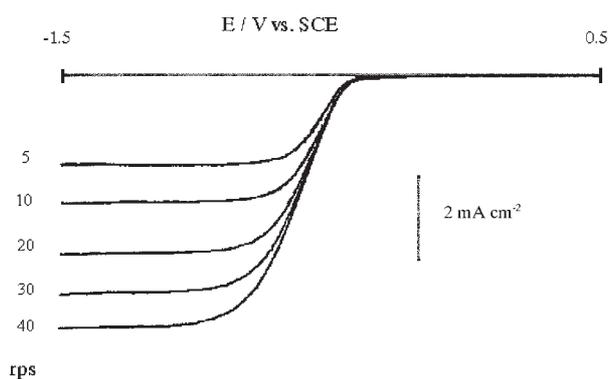


Fig. 2. The voltammograms obtained with a smooth platinum rotating disc electrode in the solution 0.01 M HCl in DMSO + 0.5 M KClO₄ at various rotation frequencies.

The plateaus of the voltammograms in Fig. 2 present the limiting diffusion currents at various rotation frequencies. The linear dependence of the limiting current density on the square root of rotating frequency, shown in Fig. 3, evidences that one is dealing here with diffusion currents. Thanks to the very negative potential of solvent reduction, the plateaus of the diffusion currents in Fig. 2 are much longer than is the case in aqueous solutions.

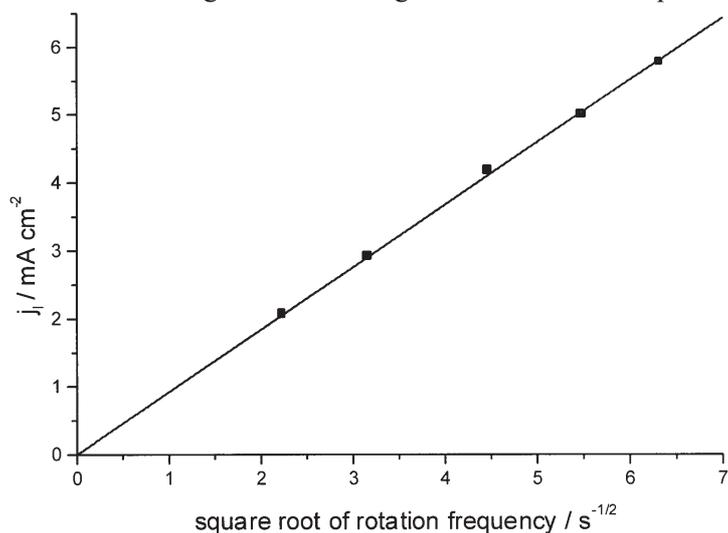


Fig. 3. Limiting current densities of hydrogen evolution on rotating platinum disc in the solutions 0.01 M HCl in DMSO + 0.5 M KClO₄ as a function of square root of rotation frequency.

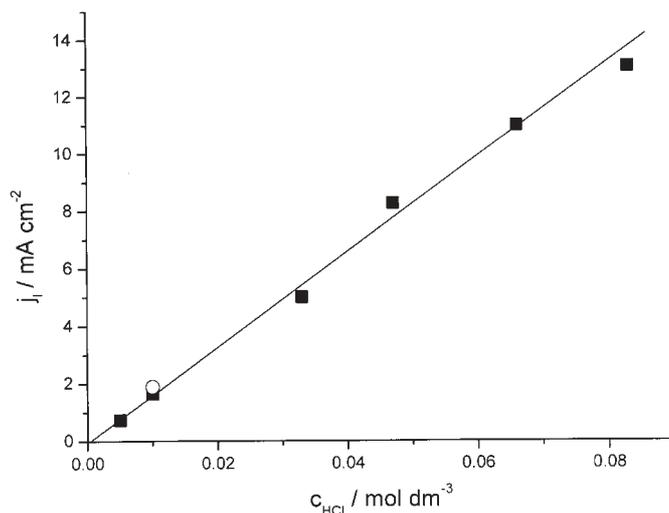


Fig. 4. The dependence of limiting current density on concentration for hydrogen evolution on platinum rotating disc in the solutions HCl (■) and HClO₃ (○) in DMSO + 0.5 M KClO₄, at the rotation frequency of 5 rps.

The limiting current density at a fixed rotating frequency is presented in Fig. 4 as a function of the HCl concentration. This dependence is linear over a wide range of HCl concentrations.

The limiting current densities, together with the corresponding viscosities were used to calculate the diffusion coefficient of the H⁺ ion, on the basis of the Levich relation:

$$j_l = 0.62nFD^{2/3} \nu^{-1/6} c \omega^{1/2} \quad (2)$$

where ν presents kinematic viscosity, *i.e.*, viscosity divided by density, and ω is angular rotation frequency ($\omega = 2\pi f$, where f is rotation frequency).

For HCl concentrations lower than 0.05 M, the density and viscosity were found to depend only slightly on the HCl concentration, and therefore the representative values of $1.141 \pm 0.001 \text{ g cm}^{-3}$ and $0.00285 \pm 0.00001 \text{ Pa s}$ were used for all HCl concentrations. For sake of comparison, these values are 1.101 g cm^{-3} and 0.00196 Pa s for pure DMSO. On the basis of these values, a mean value of the proton diffusion coefficient was calculated to amount to $4.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. Such a value is otherwise characteristic of ions in liquid solutions which do not display an abnormal mobility. For instance, for the DMSO + 0.8 M NaClO₄ solution, Giordano *et al.*¹² found the diffusion coefficient of iodide ion to be $6.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, while Nakagawa *et al.*¹⁹ have found the diffusion coefficient of Ag⁺ ion in DMSO + 1 M KClO₄ to be $2.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

The value of proton diffusion coefficient found in this work is remarkably higher than the value of $(2.76 \pm 0.06) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ found chronocoulometrically by Treimer *et al.*¹² in 1.39–2.03 mM 4-methylbenzenesulfonic acid in DMSO + 0.2 M tetraethylammonium perchlorate. The high absorption ability of both tetraethylammonium perchlorate and methylbenzenesulfonic acid may be responsible for this discrepancy.

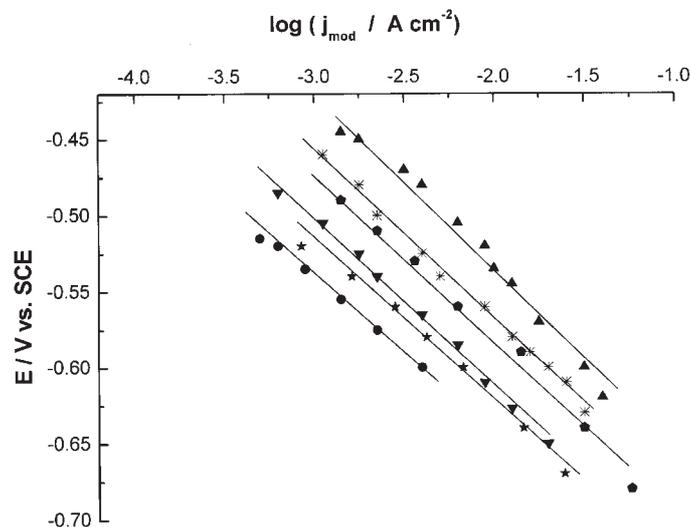
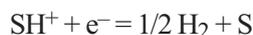


Fig. 5. Tafel plots of electrode potential, E , versus $\log j_{\text{mod}}$ ($j_{\text{mod}} = j / (1 - j / j_1)$), for hydrogen evolution on rotating platinum disc from the HCl solutions of the following concentrations (from left toward right): 0.0033, 0.005, 0.0066, 0.01, 0.033 and 0.066 M HCl in DMSO + 0.5 M KClO_4 .

As already suggested on the basis of cyclic voltammetry,^{13,14} hydrogen evolution in the system under investigation is not a pure Nernstian process. This is also evident from Fig. 2 since the half-wave potential of hydrogen reduction shifts toward negative values with increasing rotation frequency. Therefore, the I - E curves were subjected to a Tafel analysis. As one is dealing here with a mixed activation/diffusion controlled process, a rectilinear plot within an extended potential range was obtained by plotting the potential versus $\log [j / (1 - j / j_1)]$.

The lines obtained for a HCl concentrations range from 0.0033 M to 0.066 M, are presented in Fig. 5. According to the best linear fit, the slopes of the lines in Fig. 5 amount to 110 mV per decade. Under the obvious absence of any coupled processes, this indicates that, most probably, the Volmer reaction presents the slow step of the hydrogen evolution.

Since, as the literature data shows, the perchlorate ion originating from the KClO_4 supporting electrolyte is a weaker base than DMSO,²⁰ the hydrogen ion exists in the solution in the form of a solvocomplex, SH^+ ($\text{S} = \text{DMSO}$).¹⁴ The reduction may thus be presented by the reaction:



As in aqueous solutions, the dissociation of the solvocomplex is fast and its rate does not influence the simple Volmer mechanism of reduction.

In order to read exchange current densities, the lines in Fig. 5 may be extrapolated, in the direction of decreasing current, to attain the ordinate values which, according to the diagram in Fig. 1, present their equilibrium potentials. For example, for the HCl concentrations 0.01 and 0.005 M, the equilibrium potentials are -0.464 and -0.481 V, respectively,

and consequently, from the corresponding abscissa values in Fig. 5 being -3.22 and -3.03 , the exchange current densities may be calculated to be 0.602 mA cm^{-2} and 0.933 mA cm^{-2} , respectively. Obviously, these values correspond to a quasireversible kinetics.

The diagram in Fig. 5 allows to calculate the reaction order n of hydrogen reduction reaction, on the basis of the equation:

$$\left(\frac{\partial \log j}{\partial \log c} \right)_{E = \text{const}} = n$$

For this purpose one should draw the line parallel to the $\log j$ axis, which crosses all the lines in Fig. 5, and, using the crossing points, to construct a diagram $\log j$ versus $\log c$. The slope of this dependence, for instance for $E = -0.55 \text{ V}$, gives the reaction order to be 0.84 . More probably, in accordance with the relatively simple reaction mechanism, the reaction order is roundly 1 in this case, bearing in mind that the real Tafel region is rather short, and a considerable calculation error is easily to be made during its enlargement by help of the factor $1 / (1 - j / j_1)$.

Acknowledgement: One of the authors (S.M.) is grateful to the Ministry of Science, Technologies and Development which supported this work through the contract No. 1399.

ИЗВОД

ТЕРМОДИНАМИЧКЕ И КИНЕТИЧКЕ ОСОБИНЕ ВОДНИЧНЕ ЕЛЕКТРОДЕ У РАСТВОРУ ДИМЕТИЛСУЛФОКСИД + 1 М КСЮ₄

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Воднична електрода на граници платина/диметил сулфоксид + 0.5 М КСЮ₄ испитивана је са становишта равнотежног потенцијала и кинетике користећи НСl као извор протона. Показано је да зависност равнотежног потенцијала од концентрације следи Нернстову једначину. Волтамограми на ротирајућем платинском диску показују да је издвајање водоника из ове средине под мешовитом активационо-дифузионом контролом. Одређен је дифузиони коефицијент протона да износи $4.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. У области активационе контроле, Тафелови дијаграми имају нагиб 0.110 V што указује да је Фолмерова реакција спори ступањ.

(Примљено 12. августа 2002, ревидирано 3. марта 2003)

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