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Effects of additives on the practical electrolytic separation of H and D isotopes. I. Pt and Fe

B. DANDAPANI, B. E. CONWAY

Chemistry Department, University of Ottawa

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Electrolytic upgrading of D_2O-enriched water is used for production of 99·8% D_2O for CANDU-type nuclear reactor operation. Considerably enhanced values of the electrolytic H/D separation factor S can be achieved by employing additives such as urea or guanidine in the electrolyte and the increased S values are consequently of practical significance for the overall operating economy of D_2O cooled reactors.

The effects of additions of urea, guanidine and cyanoguanidine to aqueous H_2SO_4 and KOH solutions on the hydrogen/deuterium separation factor S at Pt and Fe electrodes have been investigated. The adsorption of urea and guanidine was studied at the platinum electrode by means of H-electrosorption measurements using cyclic voltammetry. The additives, especially urea, enhance S and values near the theoretically expected maximum for a free-proton transition state are found at Fe.

The following possibilities for the origin of the effects of urea (or guanidine) are considered: (1) Urea causes a kinetically significant change of orientation and structure of water in the double-layer; (2) urea acts as an alternative proton source to H_2O in the double-layer on account of its adsorption; (3) the adsorbed urea causes a local equilibrium enrichment of H w.r.t. D in comparison with the H/D ratio in the bulk water solution and hence gives rise to a change in S and (4) the OH-bonding frequencies in the H_2O proton-transfer transition state are changed in the double-layer due to H-bonding with adsorbed urea or guanidine.

1. Introduction

Nuclear reactor systems employing natural uranium depend on the use of 99·8% heavy water as moderator, and in most designs also as the heat-exchange fluid which, at the same time, provides a medium or relatively low neutron absorption cross-section in comparison with that of H_2O so that high neutron fluxes can be maintained. This is the basis of the CANDU design of reactors which are now achieving commercial success and economic viability. Present projections by Atomic Energy of Canada Ltd indicate that CANDU reactor operations in Canada will probably require a supply of moderately cheap D_2O to the anticipated cumulative extent of 7000 metric tons by 1980 and 22000 tons by 1985. There is hence considerable practical interest in (1) large-scale methods for initial enrichment of D from natural waters, e.g. by means of homogeneous H_2S/H_2O exchange or by catalytic $H_2/D_2O - H_2O$ exchange and (2) upgrading of degraded of D_2O already in use in nuclear reactors, or final enrichment of D_2O prepared by some initial exchange process. The electrolytic enrichment method has the well-known advantage of providing a high separation factor S.

An improvement of separation factor in practical H/D separation by even 1 over the normal value of *ca.* 9 for electrolysis at Fe in alkaline solutions makes a substantial difference in the commercial effectiveness of multiple-stage electrolysis/$H_2 - O_2$ burning separation plants for higher levels of D_2O enrichment. If the number of units in a cascade plant can be significantly diminished by enhancement of the separation factor at each stage, appreciable savings in capital outlay can be envisaged. In addition, lower temperature operation will always tend to improve S values due to the Boltzmann-Arrhenius factor. However, against this must be weighed the normally increased overpotential η and internal cell

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resistance polarization which raises operating costs in electrolytic H/D separation. The use of additives which simultaneously increase S while decreasing η is obviously desirable. In the present work, we have found some cases where these two advantages are to some extent simultaneously realized, but additives which have stronger effects in lowering η usually do so by a depolarization mechanism and are hence usually consumed in the continuous electrolysis. Diffusion of reduction products to the anode, e.g. in the case of guanidine, is no guarantee that the original material will be regenerated because chemically irreversible steps are involved in the oxidation and reduction of urea and guanidine. This can be demonstrated by the cyclic voltammetry experiments.

In the present work and in related previous work, S is defined as the ratio of the relative concentration of H and D in the gas phase to that in the liquid phase, counting all H and D-containing species. The H and D concentrations in the gas phase are determined by the values of the partial currents for H_2, HD and D_2 production but are experimentally evaluated by an analytical procedure (see below).

The large value of S in the electrolytic method arises primarily because the separation is a *kinetic* one, but S may still be varied appreciably by (1) change of electrode material ($S = 3$ at Hg; $S = 9$ to 10 at Fe); (2) change of electrode potential; (3) change of pH and finally (4) addition of additives. The purpose of the present paper is to present results on practical investigations of the latter type of effect using urea, guanidine and cyanoguanidine in aqueous acidic and alkaline media. Additives such as these are now being investigated in plant operations.

Previous theoretical work [1–6] on the significance of S has been concerned with (1) how S depends on the rate-determining step in the H_2 evolution mechanism [1, 3]; (2) how S depends on the chemisorption properties of the metal for H [1, 5] and hence, through this factor [7], on properties of the cathode metal [8] and (3) how S is determined by the molecular dynamic properties [9, 10] of the electrochemical proton-transfer transition state for various mechanisms. Comparisons have also been made of the relative rates of D_2 evolution from D_2O and H_2 from the H_2O solvent [3, 9, 11]. The factor which determines these effects are related to [3, 4] but not identical with those involved in determining S.

Dandapani and Fleischmann [12] examined the effect of cathodic pulsing on the S at Pt and found that interrupted polarization caused a decrease of S. The basis of the interrupted polarization studies was that a relaxation effect in the selective rates of D and H deposition and desorption would be expected to give rise to a change of S with frequency of pulsing. Unfortunately, no increase of S is found [12] under such conditions. The relaxation effect should arise because there is a decrease of energy of adsorption of H or D with coverage, the latter depending on pulse duration. The difference of rate of discharge of H^+ on a D-covered surface and D^+ on an H-covered surface (electrochemical desorption mechanism) has also been considered [3, 12].

The relation of S to other factors at electrode surfaces such as solvent orientation and adsorption in relation to adsorption of other species has been little studied. However, the effects of α-naphthoquinoline on S at Pt, Ag and Cu were reported by Eucken and Bratzler [13] and shown to decrease S; similar conclusions were reached by Walton and Wolfenden [14] with this compound at Ag and Hg. More recently, Rowland [6, 15] reported interesting enchancement effects of EDTA on S at Fe and steel in 20% aq. KOH while patents due to Stevens [16] disclose advantages of additions of urea, guanidine and related substances. These substances cause S to increase towards the maximum value [3, 6, 17] for a 'free proton' transition state, e.g. when the relative activation energy difference for H and D species is determined almost entirely by the zero-point energy difference in the initial state.

Iron cathodes are commonly used in plant operations for H_2/HD/D_2 separation in alkaline solution and we present first, in Part I of this work, studies on Fe and Pt. On the latter metal, the states of H adsorption are well known and changes of H adsorption caused by the presence of additives can be followed.

2. Experimental

2.1. *Systems studied*

In the present paper, we report results for the H/D separation factor from 50% H_2O/D_2O mixtures determined at platinum and iron in aq. H_2SO_4 and

KOH solutions in the presence and absence of (1) urea, (2) guanidine and (3) cyanoguanidine as additives.

2.2. *Method*

Galvanostatic measurements of *S* were made in an all-glass cell shown in Fig. 1 designed specially to avoid any contamination by grease but in which gases could be collected under vacuum. Only O-ring joints and Teflon stopcocks were used in the construction of the cell and gas-collection manifold up to the first liquid-N_2 trap. The cell was thermostated at 25°C by circulation of controlled-temperature water through an annular glass jacket surrounding the cell. The electrolytically evolved gas mixture (mainly H_2 + HD) was collected by means of an automatic Toepler pump and stored in a small gas collection tube (after having been dried in liquid N_2) from which samples could be taken to a gas chromatograph.

Determination of the H/D ratio in electrolytically generated H_2 is most conveniently made by means of a mass-spectrometer but, for accurate results, a special instrument must be maintained only for such measurements. An advanced mass-spectroscopic technique has been described by Hammerli and Olmstead [18]. In the present work, this approach was not possible, so that a chromatographic technique was employed.

The ratio of HD/H_2 * was determined chromatographically by separation in a 5·5 m column of chromia-coated Al_2O_3 maintained in liquid N_2. After separation of the gases by the column, the H_2/HD components were converted to H_2O and HDO vapors by passage through a CuO furnace at *ca.* 450°C. This gives better sensitivity [19] for the detection of the two components by the thermal conductivity gauge. The composition of the isotopic water vapour mixture was indicated from the signal from a differential Gow-Mac thermal-conductivity gauge with W-Rh filaments. Calibrations were carried out periodically on mixtures of known composition made up volumetrically from electrolytically pure H_2 and Merck, Sharpe and Dohme pure HD. A typical chromatogram illustrating the satisfactory quantitative separation of the H_2/HD molecules is shown in Fig. 2.

2.3. *Solutions*

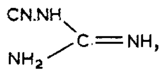
Double-distilled water from a $KMnO_4$ still was redistilled in purified N_2 [20] and used to make up solutions. D_2O was the 99.8% liquid from Merck, Sharp and Dohme which was used after a redistillation. Its purity was checked by performance of a cyclic voltammetry experiment at Pt in relation to the criteria for purity of water discussed elsewhere in a recent paper [21]. (Since the 99·8% D_2O is prepared by successive electrolysis and combustion, it does not contain the organic steam-volatile impurities now commonly present [21] in laboratory distilled water).

B.D.H. Aristar H_2SO_4 was employed directly as electrolyte (1 N) in the acid solution work while 'AR' grade KOH was employed for the work in alkaline media (1 N in KOH).

All solutions and the cell were outgassed by bubbling purified N_2 for several hours before commencement of electrolysis runs.

2.4. *Additives*

(1) Urea was the Fisher Certified ACS Reagent Grade material and was used without further purification; (2) guanidine was used as the carbonate salt (Aldrich Chem. Co); (3) Cyanoguanidine,



$$\begin{matrix} \text{CN.NH} \searrow & \\ & \text{C}=\text{NH}, \\ \text{NH}_2 \nearrow & \end{matrix}$$

was the Eastman Kodak reagent material.

2.5. *Electrical Systems*

Electrodes of thermocouple grade Pt wire were sealed into Pyrex tubes provided with O-ring seal joints at the upper end (see Fig. 1). An internal reference electrode of $\alpha + \beta$ PdH was employed in order to eliminate connecting bridges or the necessity for H_2 bubbling. Use of Hg_2SO_4 or HgO reference electrodes was avoided owing to the facility with which contamination by traces of electrodeposited Hg at the working cathode can arise when such electrodes are employed. Electrode potentials during the separation factor electrolyses were measured on a Radiometer pH-mV meter and

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* D_2 was not detectable chromatographically in the present experiments. Its level was therefore probably less than 2%.

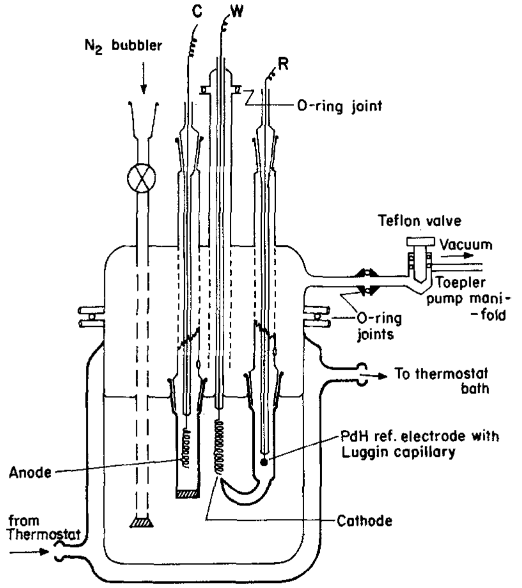


Fig. 1. The all-glass cell with O-ring joints used for separation factor measurements. C = counter electrode, W = working electrode (cathode) and R = reference electrode.

currents were measured on a Sensitive Research micromilliammeter.

2.6. *Cyclic-Voltammetry*

Potentiodynamic current-potential profiles were measured on Pt electrodes (1) to check purity of solutions and surfaces (cf. [18]) and (2) to determine the effects of adsorption of urea and guanidine. The procedure and apparatus has been described previously [22].

2.7. *D-content of Solutions*

In preparing the solutions of 50% D-content, allowance was made for the H contributed from H_2SO_4 at 1 N concentration. Similarly, in the urea solutions above and including 1 M in concentration, allowance was made for the addition of four exchangeable H's per mol.

The relatively high initial D-content was necessitated by the fact that S becomes difficult to determine accurately, especially when S is high, if H_2O is the major constituent of the solvent; then H_2 is the main gaseous component and the ratio $(H_2)/(HD)$ is inconveniently large for analysis.

2.8. *Reproducibility of Results*

Measurements of S present formidable difficulties with regard to reproducibility on account of problems of representative gas sampling and the relatively long times of electrolysis required for collection of the required volumes of gas samples. For example, at 10^{-3} A cm^{-2}, the gas evolution rate is *ca.* 10^{-4} cc sec^{-1} cm^{-2}. Fortunately, the chromatographic method diminishes the latter difficulty somewhat as only *ca.* 3 ml of gas at S.T.P. are required. The chromatographic method gives, over a short interval of time, directly, the ratio of H_2, HD and D_2 in the thermal-conductivity detector and hence has advantages over individual static determinations of thermal conductivity which require frequent calibrations and larger gas volumes. The most difficult factor in the chromatographic measurements is evaluation of peak areas with respect to appropriate base-lines, especially when tailing occurs. Some of the difficulty can be diminished if separate calibration samples of H_2 and HD are run at the same flow rate, so that overlapping between the tail of H_2 and the front of HD can be allowed for. Repetition of chromatographic runs on 'synthetic' samples of known HD and H_2 content gives reproducibility of 3% between successive determinations.

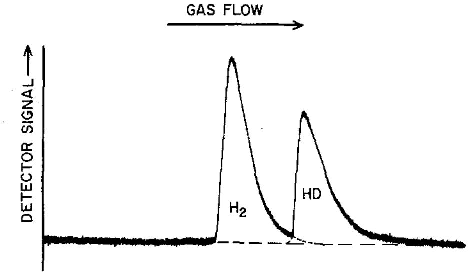


Fig. 2. A typical chromatogram of H_2/HD by using chromia-coated alumina column.

Small samples which have to be presented to the chromatograph at low pressure are less well-resolved due to some initial mixing with the carrier gas when the sample valve is turned to the carrier stream.

3. Results

The results on separation factors will first be presented, then the related Tafel parameters for H_2 evolution on the same electrodes under the same conditions. Finally, the adsorption behaviour of

Table 1. *Separation factors for H_2/HD in aq. 1 N H_2SO_4, 50·0% D at 25° C in the presence of various concentrations of urea*

	Concentration of urea in mol. l^{-1}					
$A\,cm^{-1}$	*Nil*	*0·01*	*0·1*	*1·0*	*5·0*	*10·0*
0·001	5·41 ± 0·27	5·37 ± 0·14	5·42 ± 0·32	6·29 ± 0·91	7·34 ± 0·61	8·89 ± 0·51
0·003	4·94 ± 0·16	6·72 ± 0·73	5·04 ± 0·08	7·25 ± 0·22	7·87 ± 0·75	8·39 ± 0·65
0·010	5·66 ± 0·41	7·66 ± 0·36	6·30 ± 0·44	7·38 ± 0·17	6·73 ± 0·09	7·65 ± 0·54
0·013	6·64 ± 0·44	7·69 ± 0·29	6·19 ± 0·57	7·15 ± 0·83	6·95 ± 0·34	7·55 ± 0·27
0·016	6·51 ± 0·76	7·87 ± 0·14	6·48 ± 0·65	7·12 ± 0·21	6·66 ± 0·08	8·04 ± 0·49
0·020	6·35 ± 0·27	7·05 ± 0·43	6·33 ± 0·29	6·73 ± 0·44	6·67 ± 0·07	7·06 ± 0·17
0·050	7·02 ± 0·13	7·02 ± 0·17	7·33 ± 0·40	7·21 ± 0·09	6·62 ± 0·24	7·47 ± 0·27
0·100	7·30 ± 0·63	7·77 ± 0·35	7·92 ± 0·16	7·40 ± 0·37	6·37 ± 0·14	7·11 ± 0·79
0·200	7·44 ± 0·26	7·20 ± 0·19	7·67 ± 0·23	6·95 ± 0·21	6·10 ± 0·15	7·54 ± 0·41

Table 2. *Values of $S_{H/D}$ for iron electrodes in 1 N aq. KOH (25° C) with urea*

	Area concentration			
cd $A\,cm^{-2}$	*0·0*	*1·0 M*	*5·0 M*	*10·0 M*
0·001	8·29 ± 0·93	10·47 ± 0·62	13·74 ± 0·62	13·72 ± 0·40
0·005	10·66 ± 0·46	13·27 ± 0·41	13·70 ± 0·31	13·78 ± 0·60
0·01	10·80 ± 0·69	11·58 ± 0·48	14·33 ± 0·56	13·33 ± 0·53
0·02	9·75 ± 0·41	11·01 ± 0·26	14·51 ± 0·15	13·52 ± 0·35
0·05	9·75 ± 0·24	10·63 ± 0·07	14·07 ± 0·64	14·01 ± 0·69
0·10	9·27 ± 0·39	10·31 ± 0·35	13·72 ± 0·67	14·52 ± 0·53

Table 3. *Values for $S_{H/D}$ for Pt in 1 N aq. H_2SO_4 (25° C) with addition of guanidine and cyanoguanidine*

cd $A\,cm^{-2}$	0·0	*Concentration* *0·17 M guanidine*	*0·17 M cyanoguanidine*
0·013	6·64 ± 0·44	7·51 ± 0·3	6·59 ± 0·62
0·016	6·50 ± 0·50	7·16 ± 0·83	6·43 ± 0·45
0·020	6·09 ± 0·65	7·97 ± 0·57	5·99 ± 0·22

Table 4. *Values for $S_{H/D}$ for Fe with and without guanidine and cyanoguanidine*

cd $A\,cm^{-2}$	0·0	*Concentration* *0·17 M guanidine*	*0·17 M cyanoguanidine*
0·001	8·29 ± 0·53	9·49 ± 0·54	8·49 ± 0·35
0·0025	8·85 ± 0·44	10·83 ± 1·00	9·60 ± 0·29
0·0066	10·7 ± 0·50	9·52 ± 0·99	8·04 ± 0·77
0·01	10·8 ± 0·69	9·80 ± 0·59	7·89 ± 0·48

of urea and guanidine will be described in relation to blocking of H adsorption.

3.1. *Separation factors*

3.1.1. *Effect of urea.* Numerical mean values of *S* are shown in Table 1 for Pt, together with indications of reproducibility based on 3 separate determinations of *S* at each current-density. Only at the lowest cd's is there any substantial effect of urea even up to 10 M, despite the fact (see below) that urea has an appreciable effect on H adsorption. At the highest current densities, *S* varies surprisingly little with added urea up to 10 M. However, at zero or low urea concentrations, *S* increases appreciably with cd while in 10 M urea, *S* remains almost constant or decreases somewhat with cd; the relative behaviour at 0, 1·0 and 10 M concentrations of urea is shown in Fig. 3.

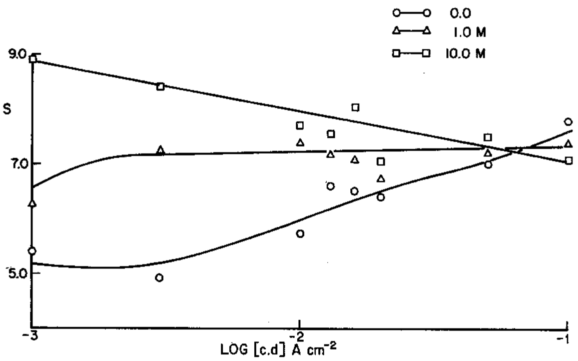


Fig. 3. Dependence of S on current density and urea concentration at platinum.

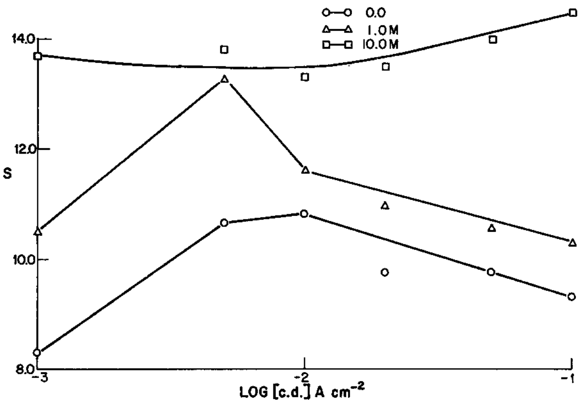


Fig. 4. Dependence of S on urea concentration and current density of iron.

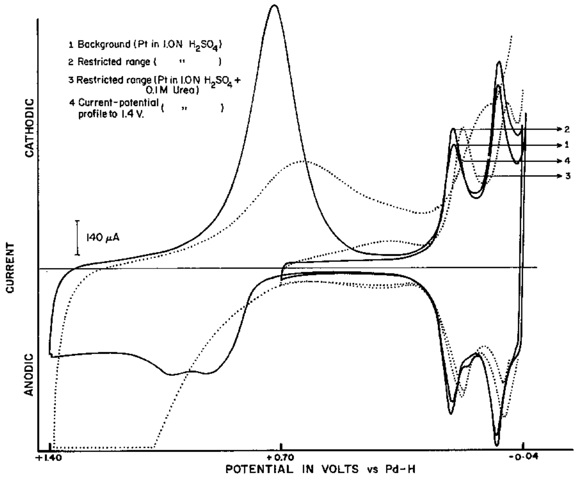


Fig. 5. Potentiodynamic i-V profile for Pt in 1·0 N H_2SO_4 with and without urea addition (0·1 M).

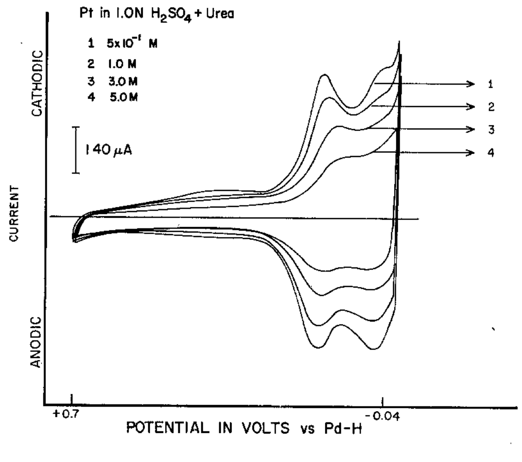


Fig. 6. Effect of additions of urea on i-V profile for Pt in 1·0 N H_2SO_4 cycled over a restricted potential range in H region.

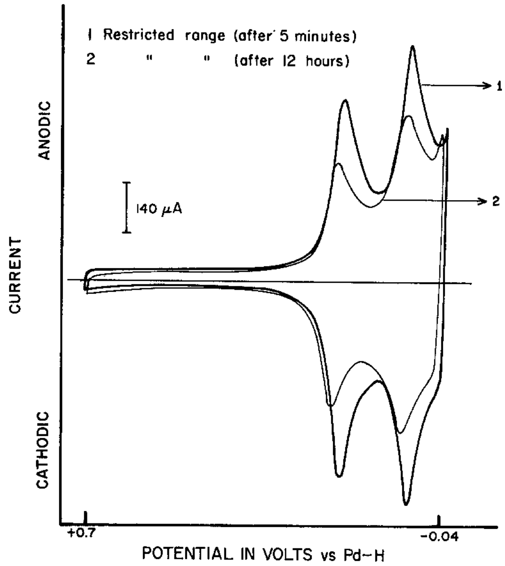


Fig. 7. Time effects on i-V profile for H region at Pt in pure 1·0 N aq. H_2SO_4.

While the effects at Pt are relatively small, the effect of urea at Fe (in aq. KOH because of corrosion problems in acid media) are much more striking, especially when concentrations of 5·0 M or greater are reached (Table 2). In the case of Fe, the S value increases more with concentration than with current density. In 10·0 M solution of urea, the separation factors are near the theoretical maximum limit for zero zero-point energy difference in the H and D-transition states. The dependence of S on log (cd) is shown in Fig. 4; the maxima for zero and 1·0 M in urea concentration are significant. For 5·0 and 10·0 M, urea, however, S becomes relatively independent of c.d.

3.1.2. *Effects of guanidine and cyano-guanidine at Pt and Fe.* A single concentration, 0·17 M, of guanidine was employed in runs with Pt. Data at three current densities are shown in Table 3. *S* is raised significantly. Cyano-guanidine has no significant effect, although it might be expected that this substance would be at least as strongly adsorbed at Pt as are acetonitrile and benzonitrile [23].

Data for Fe in 1 N aq. KOH are shown in Table 4 for 0·17 M guanidine and cyanoguanidine. The overall effects are less than with urea.

3.2. *Potentiodynamic sweep behaviour: effects of additives on H adsorption at Pt*

3.2.1. *Urea.* The potentiodynamic *i*-V profiles for Pt in 1·0 N aq. H_2SO_4 and with 0·1 M urea present are compared in Fig. 5. Figure 6 shows the behaviour up to 5·0 M in urea. Definite effects of urea on H adsorption are seen at 0·1 M and substantial effects at higher concentrations. That the observed blocking of H adsorption is not due to the well-known [21] effects of impurities in the solvent is demonstrated in Fig. 7 which shows the *i*-V profile in the H-adsorption region for restricted range (positive limit +0·7 V, E_H) cycling over a period of 5 min or 12 h. These results demonstrate (cf. reference [18]) that under conditions where the electrode is *not* repetitively cleaned by anodic oxidation at potentials >0·9 V E_H, the surface remains clean during a time period well beyond the duration of an experiment with urea additions (5 min).

If, in the presence of urea, the potential is taken into the oxide region at Pt (>0·9 V), the urea is oxidized and the intermediate formed is reduced in the H region (dotted line in Fig. 5). In alkaline solution at Pt, oxidation of urea occurs at the oxidized Pt surface (>0·9 V) but cycling in a restricted range over the H-region shows (Fig. 8) that there is little adsorption of urea itself (compare background curve for 1·0 N aq. KOH) in the alkaline solution case.

From these results, it is to be concluded that at low concentrations (up to 0·1 M) there are only small effects of urea on H-adsorption but at higher concentrations (investigated in acid) the effects are substantial. Under such conditions, *S* is also changed (see Fig. 3).

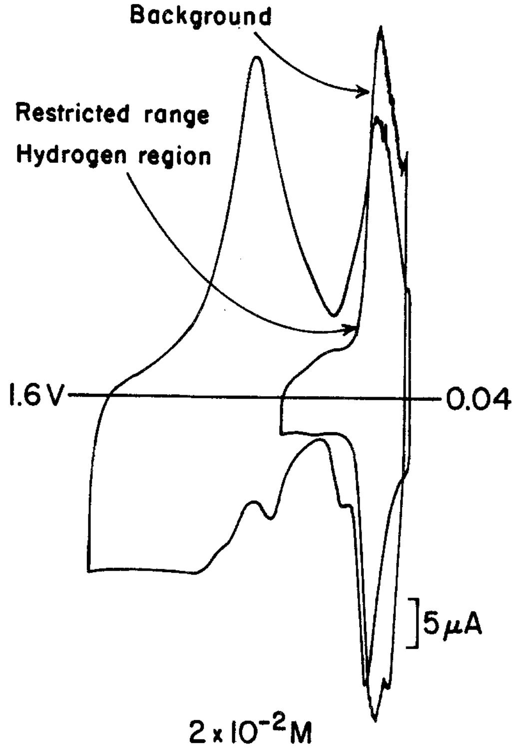


Fig. 8. Potentiodynamic *i*-V profile for Pt in 1·0 N aq. KOH with additions of urea (2×10^{-2} M).

3.2.2. *Guanidine.* Figure 9 shows the effects of progressively increasing concentrations of guanidine on H adsorption at Pt in 1 N aq. H_2SO_4 where the additive is present as the guanidinium cation. The adsorption is much stronger than that of urea and large effects arise already at *ca.* $10^{-4} - 10^{-3}$ M. In acid, the guanidine is not oxidized in the oxide region at Pt.

In 0·1 N aq. KOH solution, relatively less blocking of H adsorption occurs (Fig. 10) but extensive oxidation now occurs in the oxide region. Over a restricted range of potentials (Fig. 11) in the cyclic-voltammetry, 2×10^{-3} M guanidine blocks the strongly bound H but this effect seems to originate from a shift of H adsorption to more negative potentials. This displacement effect, already seen in Fig. 10, is hence not due to the oxidation products of guanidine. The effects are reminiscent of specifically adsorbed Cl^- ion at Pt.

The adsorption effects of guanidine are larger than those of urea, and for acidic solutions, the effect of guanidine on *S* is also larger than that of urea at a corresponding concentration. It is of

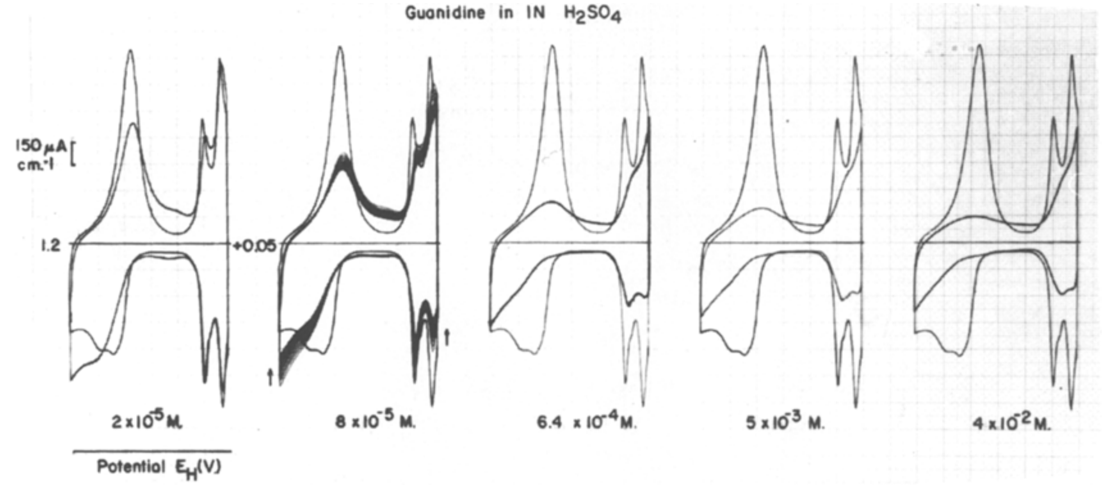


Fig. 9. Potentiodynamic *i*-V profile for Pt in 1·0 N aq. H_2SO_4 with and without additions of (different concentrations of) guanidine.

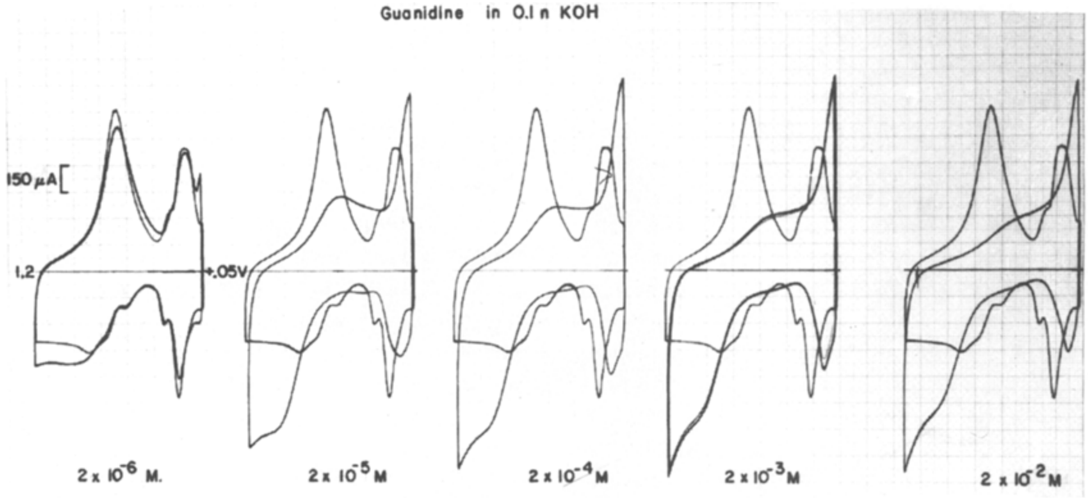


Fig. 10. Potentiodynamic *i*-V profile for Pt with progressive additions of guanidine in 0·1 N aq. KOH.

interest that, surprisingly enough, addition of guanidine to 0·1 N KOH from which H_2 is being evolved at Pt at a low rate, does not change the rate significantly although the H-adsorption is markedly changed (Fig. 12). This gives some confirmation to conclusions arising in other work that the adsorbed H seen in cyclic voltammetry work is not the H kinetically involved in H_2 evolution.

3.3. *Current-potential behaviour*

In order to characterize the *S* behaviour in terms of the overall current-potential behaviour of the Pt and Fe electrodes, a series of Tafel relations was measured at various concentrations of urea and guanidine.

3.3.1. *Platinum.* The background Tafel line for Pt in H_2SO_4 requires careful characterization as it is easily changed by the presence of impurities or changes of electrode surface condition. For active Pt electrodes in solutions made up in pyrodistilled water [21], the 30 mV slope characteristic of H recombination controlled kinetics [24] is obtained.

In the presence of various concentrations of urea, the current-potential relations are as shown in

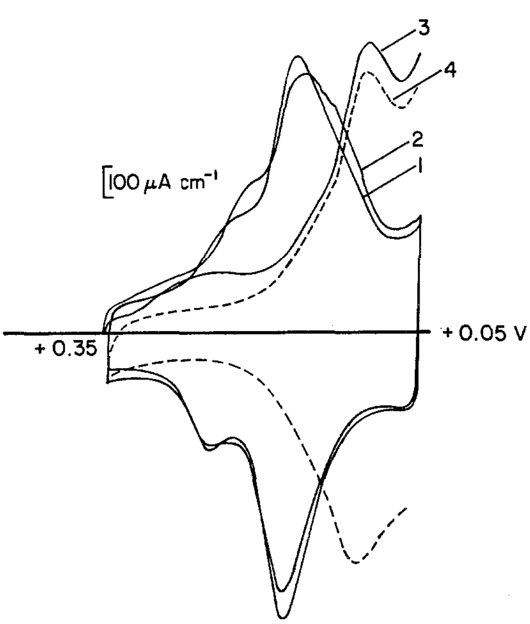


Fig. 11. Potentiodynamic i-V profile in a restricted range in the presence and absence of guanidine in KOH. 1 and 2: First and second cyclic sweeps at Pt. in 0·1 N aq. KOH; 3 and 4: third and fourth cyclic sweeps at Pt in 0·1 N aq. KOH in the presence of 2 × 10^{-3} guanidine.

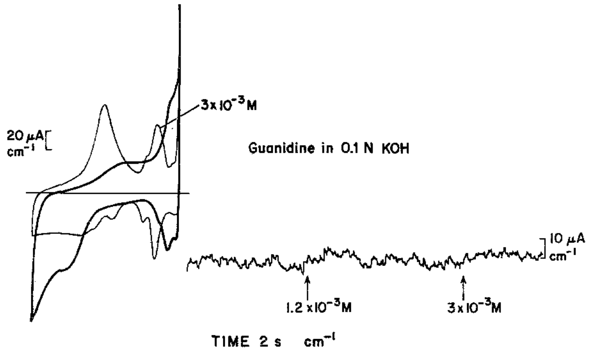


Fig. 12. Lack of effect of guanidine on the initial hydrogen evolution current near the reversible H_2 potential at Pt in relation to the blocking effect on H coverage at more positive potentials.

Fig. 13. The initial slopes of the overpotential-log (current density) lines change at urea concentrations > 0·05M, and the limiting currents tend to occur at lower current densities indicating that the limiting currents are not diffusion-controlled (cf. reference [21]).

With guanidine, the slopes of the log (current)-potential curves are increased with increasing guanidine concentration but a depolarization presumably due to guanidine reduction sets in at low current densities.

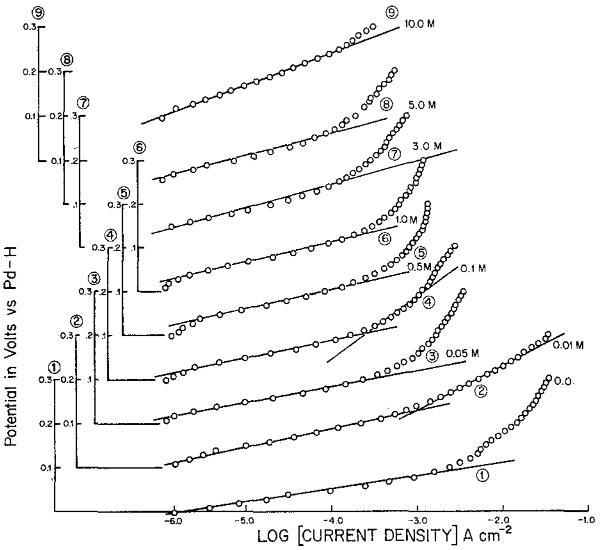


Fig. 13. Current-potential relations for H_2 evolution at Pt in aq. 1·0 N H_2SO_4 with addition of urea at different concentrations.

3.3.2. *Iron.* While impurity effects at Fe are probably less critical than at Pt, the question of effects of penetration of discharged H into Fe was considered to be a possible complicating factor. However, runs based on 26 points over increasing cathodic potentials and 26 over decreasing values showed that there was no significant hysteresis in the Tafel relation. The data in Fig. 14 are hence not materially dependent on effects of H sorption.

A family of Tafel relations was determined for Fe in 1 N aq. KOH with additions of urea to various concentrations up to 10·0 M. The results can be conveniently displayed by plots of the Tafel constants a and b, and log i_0, the exchange current density, against concentration of urea, (Fig. 14). Urea is relatively more active in its effect at Fe in low concentration. This trend is also found in some of the other results with urea.

At iron, the log (current)-potential relation normally shows *two* linear regions but the one of lower slope tends to be eliminated at the expense of the higher slope region with increase of urea concentration.

4. Discussion

4.1. *Speculations on origins of the effects of urea*

The following possibilities for the origin of an enhancement in S values due to urea were considered:

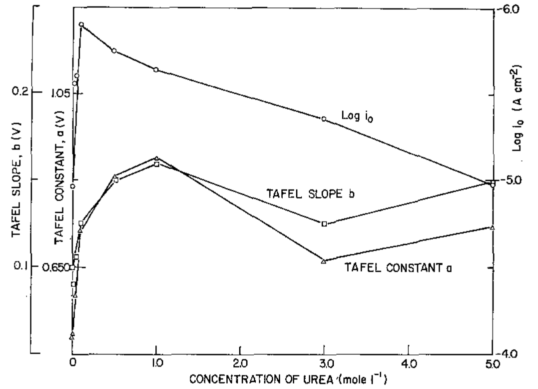
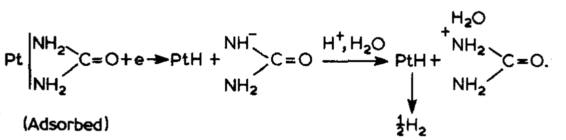


Fig. 14. Plots of Tafel constants a, b, and log i_0 for Fe in 1·0 N aq. KOH against concentration of urea.

(1) That urea changes the water structure in the double-layer and modifies both the state of the reactant H_3O^+ or H_2O in acid or alkaline solution, and the transition state. The effect of urea is already appreciable at 0·1–1·0 M and this can be reconciled with its appreciable adsorption demonstrated in the case of platinum (Figs. 5 and 6). We may anticipate similar strong adsorption at Fe owing to the transiton-metal character of the latter element.

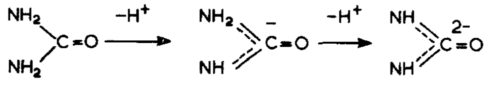
The effects of urea on water structure and H-bonding are well known and have been examined by various workers [25, 26] and interpreted in terms of competitive H-bonding. In connection with the present work, the partial molar volume and adiabatic compressibility of urea in aqueous solutions in H_2O and D_2O were determined by Mathieson and Conway [26]. For electrostricting salts, urea (3 M) increases the partial molal compressibility of NaCl, NaBr and Pr_4NBr, the value for the latter salt changing from −8·0 to +19·1 ml mol^{-1} bar^{-1}. These results indicate that urea destructures water and prevents the structure-forming tendency of Pr_4N^+ ion (normally observed with pure water as solvent) to be realized.

(2) The urea acts as a proton source alternative to H_2O in alkaline solutions, behaving in its adsorbed state as a mediator in proton transfer. In other work [27] we have demonstrated that urea can be an electrochemical proton source since H_2 can be cathodically evolved from (i) molten urea containing a small quantity of KOH as electroyte and (ii) from a urea solution in acetointrile containing $NaClO_4$ as electrolyte, well below the decomposition potential of the $NaClO_4/CH_3CN$ system itself. The mediator mechanism could be:



The possibility that urea is adsorbed competitively with H_2O is also indicated by the values of dipole moments per unit volume for urea and water. Taking $\mu = 4{\cdot}56$D for urea and the partial molar volume [23] as 44 ml mol^{-1}, the moment per unit volume is 1·03 D mol ml^{-1} which is close to the value for water based on a moment of 1·87 D.

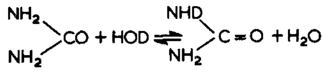
The cathodic reaction of urea would be represented by:



following an electron transfer giving H_2 at the cathode. The anion(s) of urea can be stabilized by resonance like those of guanidine, as discussed by Gund [28] but in water will normally be rapidly reprotonated.

In relation to these possibilities, there are similarities between urea and guanidine involving so-called Y-delocalization and a 6-π orbital system [28]. The situation is as shown above. The delocalized π-electron character of the urea anions may facilitate adsorption at transition metals with complete d-bands (Fe, Pt). Increasing π-delocalization accompanies substitution of N for O, as with guanidine in comparison with urea. The dianion of urea is similar to and isoelectronic with trimethylenemethane where the Y delocalization occurs with maximum facility.

(3) In addition to effects (1) and (2), but related to the rate of the pathway through process (2), it is necessary to consider any enrichment in H or D by the adsorbed urea. If relative H enrichment occurs in the equilibrium:



and discharge occurs from urea molecules, then an enhancement of S can arise for equilibrium thermodynamic reasons in addition to any kinetic effects. Alternatively, if urea or guanidine change the equilibrium

$$2HOD \rightleftharpoons H_2O + D_2O$$

in the electrode interphase more than they do in solution, but discharge still occurs from H_2O adsorbed in the double-layer, then a change of S could also arise.

4.2. *Relation to mechanisms of H_2 evolution*

The effect of urea on S for Fe electrodes in alkaline solution must be considered in the light of the hydrogen evolution at Fe. In acid media, Bockris and Koch [29] have given evidence that the primary electron transfer-proton discharge step is rate-determining. While the identification of the mechanism of the h.e.r. at Fe is difficult in acid medium, comparison of relative rates of H_2 and D_2 evolution enabled Bockris and Koch to reach the above conclusion. In alkaline solution, the stoichiometric number can be determined and is found to be 1. This leads [26] to the possibility that either the proton transfer step itself or the atom-ion desorption is rate-controlling. Since there is some* indication [26] that the proton transfer step is rate determining in *acid* medium, it is likely to be 'more' rate-controlling in alkaline solutions due to the usually greater difficulty of proton discharge from H_2O than from H_3O^+.

Hence the enhancing effect of urea on S must be connected with (1) a change of the H_2O transition state in the presence of urea or (2) involvement of a new transition state for proton transfer from urea itself, rather than with changes of H coverage since normally $\theta_H \ll 1$ for rate-controlling proton transfer.

A rationalization for kinetic effects arising from structure-changing solutes in water on S_{HD} will lie, in part, in the modification of intra (and inter) molecular frequencies ν which such substances can cause on account of changes of H-bonding. The largest effects will arise in the asymmetric stretch mode in the initial state. Hydrogen bond scission which can arise due to a structure-breaking solute such as urea, can lead to a maximum change of ν of *ca.* $+400\,cm^{-1}$ [30] for non-H-bonded OH groups. This corresponds to an increase of zero-point energy of the bond of *ca.* $520\,cal\,mol^{-1}$. Effects in bending modes are in the opposite direction but substantially smaller [31]. This change in zero-point energy could give a maximum increase in $S_{H/D}$ by a factor of *ca.* 1·28, e.g. the factor arising [32] from $\exp(520 - 520/\sqrt{2})/RT$ for discharge from H_2O and D_2O. This factor of 1·28 or *ca.* 30% in S is of the right magnitude in comparison with experiment, but due to the complexities of calculations [32, 33] of separation factors for H-bonded solvents, it cannot be regarded as more than a semi-quantitative estimate of the main effect that may arise.

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* Although the H_2 evolution reaction has been extensively studied at Fe and Ni, it must be recognized that the diagnostic kinetic data that can be obtained for these metals still leave some ambiguity with regard to mechanism, viz. whether the initial proton discharge or the H-atom/ion desorption (H at low coverage) step is rate-controlling.

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