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Abstract

The autoprotolysis constant K_{HS} of formic acid/water mixtures as solvent has been calculated from acid-base potentiometric titration curves. A correlation of the acidity scale pK_{HS} of each media vs. that of pure water has been implemented owing to the electrochemical redox function $R°(H^+)$ of Strehlow. The results show that formic acid/water mixtures are much more dissociated than pure water; they are sufficiently dissociated media to allow electrochemical measures without addition of an electrolyte. It has also been shown that for a same H^+ concentration the activity of protons increases when formic acid concentration grows. For more than 80% by weight of formic acid the acidity is sufficiently increased so that the whole acidity scale pK_{HS} is in the super acid medium of the generalized acidity scale pH_{H2O}.

Keywords: acidity scale; autoprotolysis constant; formic acid; formic acid/water mixtures; redox function.

1. Introduction

Chemical and electrochemical properties of non aqueous solvents have been widely studied in the past and mainly since 1960 [1-5]. The main reason was to probe new chemical and electrochemical possibilities in liquid media out of water limitations. This knowledge

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acquired by a lot of researches led to important developments in the area of electrochemical energy storage with implementation of new batteries, more powerful and reliable, at first mainly devoted to military and spatial applications but rapidly also for civil applications. For these new electrochemical devices lithium was chosen as anodic material because of its very low volumic mass (0.534 g cm^{-3}) but overall owing to its very high massic capacity (3860 Ah kg^{-1}). But as lithium is the most electropositive metal (-3.01V/NHE), its use in water was not possible, and new electrolytes had to be selected. Among all aprotic solvents available, some of them like propylene carbonate, dimethoxyethane, acetonitrile, have been chosen to implement lithium batteries[6-7]. Nowadays these batteries have invaded our daily environment (watches, computers, cellular phones, camcorder,…).

If researches on non aqueous solvent properties have strongly decreased last years, new challenges boost some of them. It is the case, in the area of electrical energy production, for implementation of usable and reliable fuel cells. In this area the main problem is hydrogen storage and delivery for a hydrogen/oxygen fuel cell. For security reasons, one way is to produce hydrogen when necessary by reforming from hydrocarbon compounds. Another way could be to use a hydrocarbon fuel directly oxidable. The first way is the greatest challenge for fuel cells, concerning electric production for transportation vehicles and in cases where powerful sources are needed. The second way is mainly for all cases where a self and small electric power is necessary (all portable devices). In this field miniaturized fuel cells are destined to replace conventional batteries because fuel cells are able to store a much higher energy density, and overall are able to be immediately recharged by replacing the fuel cartridge. In this area, last years many works have been done on direct formic acid fuel cell (DFAFC) [8-16]. In these Polymer Electrolyte Membrane Fuel Cells (PEMFC) formic acid is directly oxidised into carbon dioxide and H^+ ions which crosses the membrane to the cathodic compartment and produce water from oxygen (air) reduction. Some advantages of formic acid

for such a use are its strong dissociation (no need of electrolyte), the high theoretical voltage of the corresponding fuel cell (1.45V for formic acid/oxygen system), and the possibility to operate with high formic acid concentrations (i.e. high energy density with respect to the fuel volume) without strong leakage through the membrane. Rice et al. [8] empirically showed that an optimum formic acid concentration must be used, around 50/50% by wt. water-formic acid mixture. Replacing platinum black electrocatalyst by a Pd/C one, Ha et al. [15] recently showed that the optimum could be a 40/60% wt.% mixture.

There is an other area where organic solvents, more precisely water/solvent mixtures, are concerned: this is all researches on salts splitting to produce acids and bases. This is mainly the recent advances on electromembrane processes which allow these new possibilities. Some studies were firstly done to solve environmental problems concerning no valuable industrial effluents like salty effluents [17-20] or too diluted one to be valuable [21]. The main objective was to purify water. But it rapidly appeared that electromembrane processes could also be useful and profitable to produce acids which are needed in chemistry, food, pharmaceutical and biodegradable polymer industries and the demand of which undergoes a very strong growth [22-26]. So the last ten years saw the implementation of several membrane processes all over the world [25]. Coupling classical electrodialysis (ED) with bipolar membranes electrodialysis (BMED) or membrane electrolysis (ME) allows production of concentrated or very concentrated solutions. For example production of nitric acid 8 mol L^{-1} from ammonium nitrate solution by a ED+ME process [18] lead to a nitric acid/water mixture 40/60% by wt..

In the area of organic acids production electromembrane processes are very interesting because in addition to production of valuable products, they are more friendly for environment; in fact they avoid precipitation steps which lead to large amounts of solid wastes in traditional processes. In all cases the industrial benefit is to produce concentrated

solutions of products. But according to the high concentrations reached these solutions are no more water solutions of acids but a new liquid medium.

The present work is devoted to the study of formic acid/water mixtures in connection with formic acid regeneration by electromembrane processes [27]. Formic acid is used in many industries such as textiles, natural rubber and leather processing. It is also used in agriculture, as well as in the production of cosmetics, disinfectants, detergents and medicines. In textile industry formic acid is mainly used in cellulose spinning. In this process further fibber washing steps lead to effluents containing diluted sodium formate. It might be valuable to split this salt to recycle concentrated formic acid. More concentrated would be the recycled formic acid, more profitable should be the recycling process.

Some works have already be done by Luo et al. [28-29] on formic acid concentration by electromembrane processes. But these authors do not really studied formic acid regeneration from formate salt but the transfer of formic acid from the diluted compartment to the concentrated one. Jaime Ferrer et al. [27] studied a whole process coupling ED and BMED for diluted sodium formate (0.1 mol L^{-1}) splitting allowing production of concentrated formic acid (7 mol L^{-1}). Problems encountered, leakages through the membranes and consequently limitation of HCOOH concentration reachable, raise questions on the physicochemical behaviour of the concentrate solution when formic acid concentration increases from 1 to 7 mol L^{-1}.

The first question concerns the degree of dissociation of formic acid/water mixtures. This point is important in electrodialysis. As formic acid is a weak acid in water ($pK_a = 3.7$), do we consider that highly concentrated solutions of formic acid remain weakly dissociated [28]? The answer may be obtained by determining the value of the autoprotolysis constant K_{HS} ($pK_{HS} = -\log K_{HS}$) of each formic acid/water solvent in varying proportions. The pK_{HS} values

may be obtained from strong acid/strong base potentiometric titrations in each solvent [30-31].

The second question concerns the acidity levels of the formic acid/water mixtures compared to pure water. A correlation of the origin of all acidity scales vs. a generalized pH_{H2O} scale (referred to pH scale in water) would allow to know the variations of proton activity during formic acid concentration. Such a correlation between acidity scales in various solvents has been widely described [4]. It would also give explanations on proton leakage observed and on corrosion power of highly concentrated formic acid solutions.

2. Experimental

2.1 *Materials*

Titrations were done with a Metrohm 736 GP Titrino apparatus. Acquisition and processing of data have been done by the TiNet 2.4 software.

Acidity was measured with a combined glass/reference electrode Metrohm 6.0299.100 Solvotrode. The reference electrode is Ag/AgCl/LiCl sat. in ethanol.

Current-potential curves were recorded with a PARSTAT® 2263 potentiostat/galvanostat from Princeton Applied Research (AMETEK Inc.). The Power PULSE® module from the Power SUITE® software was used to exploit the current-potential curves.

The reference electrode was home made. It was the $Ag/AgCl/KCl_{sat.}$ system in each water/formic acid media.

The working electrode was a platinum rotating disc electrode EDI 101 (2 mm diameter) connected with a Speedcontrol unit CTV 101 from Radiometer Analytical. For the H^+/H_2 electrochemical system the platinum disc was platinized according to the following recipe: H_2PtCl_6 3.5% + $Pb(CH_3COO)_2$ 0.005% (w/v) in water, 1000 rpm, E = -200 mV/SCE, t = 90s.

The auxiliary electrode was a platinum one from Radiometer Analytical.

Water traces in pure formic acid were controlled by Karl Fischer titration with a coulometric titrator, Aquaprocessor type, from Radiometer Analytical.

2.2 *Chemicals*

Formic acid 97% from Avocado Organics was used for the formic acid/water mixtures. Formic acid 99-100% NORMAPUR™ for analysis from VWR Prolabo was used for pure formic acid media.

Perchloric acid 70% for analysis from Fisher Chemicals, pellets of sodium hydroxide 98% and sodium formate 98% from Avocado Organics were used for acid-base titrations.

Solid potassium chloride for analysis used for the reference electrode was from Acros Organics.

Ferrocene [bis(cyclopentadienyl)iron] 99% pure was from Avocado Organics.

3. Results and discussion

3.1. Potentiometric determination of autoprotolysis constant

3.1.1. Theory

It is well-known that an amphoprotic solvent HS dissociates as

$$2\ HS \Leftrightarrow H_2S^+ + S^- \qquad (1)$$

(H_2S^+, the solvated proton also written H^+ is the strong acid; S^- is the strong base)

the autoprotolysis (or autosolvolysis) constant K_{HS} is

$$K_{HS} = [H^+][S^-] \qquad (2)$$

In formic acid/water mixtures the autoprotolysis reaction is

$$H_2O + HCOOH \Leftrightarrow H_3O^+ + HCOO^-$$

with

$$K_{HS} = [H_3O^+][HCOO^-] \qquad (3)$$

So K_{HS} value may be measured from strong acid-strong base potentiometric titration curves between the pH values for $[H_3O^+]$ = 1 mol L^{-1} (pH = 0) and for $[HCOO^-]$ = 1 mol L^{-1}, (pH = pK_{HS} = -logK_{HS}). But this measure from two experimental points is imprecise. The best way is to compute the whole titration curve and to fit it with the experimental one.

In formic acid/water mixtures perchloric acid $HClO_4$ is always a strong acid, and sodium hydroxide NaOH always a strong base [4] according to the solvolysis reactions:

$$HCOOH + HClO_4 \Rightarrow HCOOH_2^+ + ClO_4^- \qquad (4)$$

(where $HCOOH_2^+$ is the solvated proton, written H^+)

and

$$HCOOH + NaOH \Rightarrow HCOO^- + Na^+ + H_2O \qquad (5)$$

(where $HCOO^-$ is the strong base)

So NaOH or sodium formate NaHCOO may be used as a strong base in formic acid/water mixtures.

The strong acid/strong base reaction is

$$H^+ + (ClO_4^-) + OH^- + (Na^+) \Leftrightarrow H_2O + (Na^+) + (ClO_4^-) \qquad (6)$$

in pure water, and

$$H^+ + (ClO_4^-) + HCOO^- + (Na^+) \Leftrightarrow HCOOH + (Na^+) + (ClO_4^-) \qquad (7)$$

in formic acid/water mixtures.

All along the titration the electroneutrality equation is

$$[H^+] + [Na^+] = [HCOO^-] + [ClO_4^-] \qquad (8)$$

If a volume V_0 of $HClO_4$ the concentration of which is C_{HClO4} is titrated by addition of a volume V of a C_{NaHCOO} solution of the strong base, and owing to relations (2) and (7-8) the pH of the solution is obtained from the relation

$$[H^+] = \frac{-\left(\frac{VC_{NaHCOO} - V_0C_{HClO4}}{V_0+V}\right) + \sqrt{\left(\frac{VC_{NaHCOO} - V_0C_{HClO4}}{V_0+V}\right)^2 + 4K_{HS}}}{2} \qquad (9)$$

It is well-known that a pH measure with a glass electrode is in fact a membrane potential measure so that

$$[H^+] = 10^{\frac{\Delta E_{measured}}{2.3RT/F}} \qquad (10)$$

where

R is the ideal gas constant (8.314 J K^{-1} mol^{-1})

T the temperature (K)

F the faraday constant (96,485.34 C mol^{-1}).

$\Delta E_{measured}$ is the sum of all potential differences of the potentiometric chain, including that of the reference electrode. As the combined glass electrode is dipped in several different solvents (formic acid/water of various percentages) the junction potential between the reference electrode (in ethanol media) and the solution is not constant. It may vary very widely. The measured potential is then not only due to the membrane potential of the glass electrode but also to the shift of the reference electrode potential due to junction potential (constant in a given media). So what must be considered is each experimental curve vs. the calculated one, but none comparison of all experimental curves between them.

3.1.2. Results

Perchloric acid has been titrated by sodium hydroxide or sodium formate in pure water and in formic acid/water mixtures varying formic acid from 4.6 to 98.3 wt.%. Titration curves have been recorded (E = f(V)). All titration curves have been collected on a same graph (figure 1).

As foreseen the curves are gradually translated as the solvent is becoming different from water because of the additional junction potential. The potential difference values between the first part of the curves (acidic media) and the second part (basic media) is correlated with the pK_{HS} of the solvent (relations (3, 6-7)). So at first glance it appears that pK_{HS} strongly decreases from pure water (curve (1)) to pure formic acid (curve (15)), passing through a

minimum. The very small potential variations appearing on figure (1) shows that only fitting between experimental and calculated curves will allow to obtain precisely the pK_{HS} value of each solvent.

The curves are computed from relations (9) and (10), knowing C_{HClO4}, C_{NaHCOO}, V_0, V, and firstly estimating values for experimental glass electrode response (slope of straight line $\Delta E_{measured} = f(pH)$) and pK_{HS}. Calculation is done for a lot of $\Delta E/V$ couple of points (a 0.01 mL increment). Fitting between experimental and calculated curves is achieved by varying glass electrode response and pK_{HS} values till the two curves be superimposables. An example is given figure 2 where only some calculated couple of points $\Delta E/V$ are reported for a best visibility of the fitting.

Then each experimental curve is linearised for the fitted pK_{HS} value to calculate the experimental glass electrode response: slope of the straight line E_{exp} vs. pH_{calc} from relation (9). This value is then used to improve the calculated curve if the experimental slope value (2.3RT/F) is very different from that postulated. In fact these values are always close to the theoretical one at 20 °C (0.058 V) as shown in table 1.

So autoprotolysis constants K_{HS} values are obtained from fitting between experimental and calculated titration curves for each formic acid/water mixture. The corresponding values of pK_{HS} are collected table 1. Figure 3 shows the variations of pK_{HS} from pure water to "pure" formic acid (98.3% i.e. ≈1.1 mol L^{-1} residual water). The three series of experiments point out a good reproducibility of values. The curve shows a strong and rapid decrease of pK_{HS} when formic acid is added to water. pK_{HS} value is minimum for about 50/50 wt.% water-formic acid mixture and then increases again, the more when formic acid is pure. In fact a small value of pK_{HS} means a high value of the autoprotolysis constant K_{HS}, and then a great dissociation of the solvent. The graph shows that formic acid/water mixtures are more dissociated than pure water, and then are more conducting media. The maximum of

dissociation is obtained for the range 25-65 wt.% HCOOH. In 50/50 wt.% formic acid/water mixture for example the pK_{HS} value shows that $[H^+] = [S^-] = 0.07$ mol L^{-1}. In this case the conductivity increase may be enough to carry out electrochemical measurements without addition of an electrolyte.

3.2. Correlation of acidity scales

3.2.1. Theory

As shown above, the acidity scales, i.e. the number of pH units reachable in formic acid-water mixtures as solvents, strongly vary from pure water ($\Delta pH = 14$) to pure formic acid ($\Delta pH \approx 5$), passing through a minimum ($\Delta pH \approx 2.3$) for 50/50 wt.% mixture. But the origins, pH = 0 in water and in each formic acid/water mixture, are not comparable. What is obtained in each solvent (and water) is $[H^+] = 1$ mol L^{-1}. But a same concentration of H^+ ions do not imply a same activity of proton.

In a given solvent the activity of an ion i is bound to its concentration by the well-known relation $a_i = \gamma_i c_i$.

In the same way the activities of an ion i at the same concentration in water and in an other solvent are bound by the relation

$$\frac{(a_i)_S}{(a_i)_{H_2O}} = \Gamma_t(i)_{H_2O \rightarrow S} \qquad (11)$$

where $\Gamma_t(i)_{H_2O \rightarrow S}$ is the activity coefficient of solvent transfer from water to S.

Relation (11) shows that a same concentration of an ion in two different solvents do not imply a same activity in each of them. In fact there is no reason that the ion i be solvated in the same manner in water and in an other solvent, and then that its activity be the same. This problem has been largely studied in the past [4, 30, 32].

The activity coefficient of solvent transfer Γ_t allows to evaluate the differences of solvation of ions from water to non aqueous solvents. If we consider H^+ ion, its activity coefficient of solvent transfer is expressed as

$$\log\Gamma_t(H^+)_{H_2O\rightarrow S} = -\frac{\Delta G_t^0(H^+)_{H_2O\rightarrow S}}{2.3RT} \qquad (12)$$

where $\Delta G_t^0(H^+)_{H_2O\rightarrow S}$ is the molar free energy variation for H^+ ion transferred from water to solvent S (variation of solvation energy by changing the solvent).

A value of $\Gamma_t(H^+)$ higher than unity ($\log\Gamma_t(H^+) > 0$) corresponds to a solvation of H^+ more energetic in the solvent S than in water (the contrary if $\Gamma_t(H^+) < 1$). The more solvated is H^+, the less reactive it is.

A potentiometric evaluation of activity coefficients of solvent transfer has been proposed by Strehlow [33-34] through the use of ferrocene/ferricinium redox couple (ferrocene is dicyclopentadienyl iron(II)). Strehlow postulated that solvation of ferrocene and its oxidised form ferricinium (complex dicyclopentadienyl-iron(III)) are similar in all solvents. This electrochemical couple may thus be considered as an "universal" potential reference electrode in all solvents (its redox power is not influenced by change of solvents because oxidant and reducer are solvated in the same manner). Consequently Strehlow defined an experimental parameter, designated by R° (redox function), corresponding to the difference of potential measured between two electrochemical couples, one of them being ferrocene/ferricinium, in water on the one hand and in an other solvent S on the other hand, allowing to determine ion activity coefficients of solvent transfer.

If the second electrochemical couple is H^+/H_2 (hydrogen electrode) we have

$$R°(H^+)_{H_2O\rightarrow S} = \frac{-(\Delta E^\circ_{NHE/Fec})_{H_2O\rightarrow S}}{2.3RT/F} = \log\Gamma_t(H^+)_{H_2O\rightarrow S} \qquad (13)$$

where NHE is normal hydrogen electrode and Fec is ferrocene/ferricinium couple.

So the activity coefficient of solvent transfer for H^+ ion can be potentiometrically measured. This allows to correlate the acidity scales of solvents with that of water.

In water the standard potential E° for hydrogen electrode is – 0.40 V vs. Fec (Fec/Fec^+ couple). Measures of E°_{NHE} in a solvent S allows to calculate the value of $R°(H^+)$ according to (13). This value gives the shift between pH = 0 in water and pH = 0 in S. This is the difference of acidity level for pH = 0 in the two solvents.

To compare the acidity levels of all solvents (and solvent mixtures) a generalised acidity scale pH_{H2O} called $R(H^+)$ was defined. In water the acidity scale stretches from pH_{H2O} = 0 to pH_{H2O} = 14.

Some works have been done to correlate the acidity scales of water and anhydrous formic acid [31, 35-36]. A $R°(H^+)_{H_2O \rightarrow HCOOH}$ value equal to –7.4 has been estimated by Bréant et al. [31]. So the origin of acidity scale of anhydrous formic acid would be for pH_{H2O} = -7.4. Consequently the activity of proton is strongly increased in formic acid owing to its least solvation than in water. Apart from this determination for anhydrous formic acid, nothing is known about formic acid-water mixtures. It is why a correlation between the acidity scales has been achieved in order to know the variation of the acidity level of formic acid/water mixtures.

3.2.2. Results

3.2.2.1 Hydrogen electrode potential

Current-potential curves have been recorded for hydrogen system corresponding to the reaction

$2\ H^+ + 2e^- \Leftrightarrow H_2$

on platinized platinum in formic acid/water mixtures of several percentages. For each media $HClO_4$ concentration was 1 mol L^{-1} and hydrogen gas saturated the solution.

The curves are represented on figure 4. Their shapes are similar. It only appears that hydrogen solubility seems to slightly increase with formic acid concentration. More important is the potential shift (≈ +300 mV) from formic acid 6 mol L^{-1} (26 wt.%) to 26.2 mol L^{-1} (98.3 wt.%). The H^+/H_2 potential is negative vs. the reference electrode when formic acid percentage is low and became positive for high formic acid percentage. This shows that it is easier to reduce H^+ ions when formic acid concentration increases, in connection with its higher activity.

To correlate the acidity scales of water and formic acid/water mixtures, the standard potential of H^+/H_2 system must be known. This one has been calculated by fitting theoretical and experimental curves in each media.

Theoretical current-potential curves are calculated from the Butler-Volmer relation applied to the hydrogen system [37]:

$$I=\frac{\frac{k^\circ}{(k_D)_R} I_R \, 10^{\frac{\beta(E-E^\circ)}{2.3RT/2F}} + \frac{k^\circ}{(k_D)_{Ox}} I_{Ox} \, 10^{\frac{-\alpha(E-E^\circ)}{2.3RT/2F}}}{1+\frac{k^\circ}{(k_D)_R} 10^{\frac{\beta(E-E^\circ)}{2.3RT/2F}} + \frac{k^\circ}{(k_D)_{Ox}} 10^{\frac{-\alpha(E-E^\circ)}{2.3RT/2F}}} \qquad (14)$$

where

k° is the standard rate constant (cm s^{-1})

k_D is the diffusion rate constant (cm s^{-1})

α and β are the transfer coefficients for reduction of H^+ and oxidation of H_2

I_R and I_{Ox} are the limiting currents for oxidation and reduction

E° is the standard potential of the H^+/H_2 system.

The theoretical current-potential curves have been calculated assuming that $\alpha = \beta = 0.5$, $I_{Ox} >> I_R$ ($I_{Ox}/I_R \approx 1000$) and $2.3RT/F = 0.06V$ for postulated $k°/k_D$ and $E°$ values. Then $k°/k_D$ and $E°$ parameters are varied until superposition of experimental and calculated curves. Fitting between experimental and calculated curves is very good for each media, as shown on figure 5 for three of them (only some calculated I/E couple of points are reported). The standard potentials thus obtained are collected in table 2.

3.2.2.2. Ferrocene/ferricinium potential

Correlation of acidity scales through relation (13) needs knowledge of the standard potential of ferrocene/ferricinium couple. According to Strehlow this one may be considered as a reference potential system valid in all solvents (independent of solvation).

The standard potential $E°$ of the reaction

$$Fec - e^- \Leftrightarrow Fec^+$$

where Fec is dicyclopentadienyl-iron(II) is obtained from fitting between experimental and calculated current-potential curves of ferrocene oxidation. This theoretical curve is calculated from the Nernst relation applied to equilibrium at electrode interface

$$E = E^o + \frac{2.3RT}{F} \log \frac{[Fec^+]_{el}}{[Fec]_{el}}$$

where $[Fec^+]_{el} = \frac{I}{d_{Fec^+}}$

$$[Fec]_{el} = \frac{I_{Fec} - I}{d_{Fec}}$$

d_{Fec} and d_{Fec^+} are the diffusion coefficient of ferrocene and ferricinium species.

Then

$$I = \frac{I_{Fec}\, 10^{\frac{E-E_{1/2}}{2.3RT/F}}}{1+10^{\frac{E-E_{1/2}}{2.3RT/F}}} \qquad (15)$$

with $E_{1/2} = E° + 2.3\frac{RT}{F}\log\frac{(k_D)_{Fec}}{(k_D)_{Fec^+}} \approx E°$

Current-potential curves for ferrocene oxidation have been recorded in several formic acid/water mixtures (figure 6).

The half-wave potentials $E_{1/2}$ for each media are collected in Table 3. From these values and those of standard potentials of H^+/H_2 system the redox function of transfer of H^+ ion from water to formic acid/water mixtures, $R°(H^+)$, is calculated according to (13) (Table 4).

3.2.2.3. $R(H^+)$ scales

Owing to these $R°(H^+)$ values and to the pK_{HS} values determined by titration, the water-formic acid mixing diagram is drawn (figure 7). This diagram shows what is the variation of the acidity limit from pure water, $R°(H^+)=0$, to pure (98.3 wt.%) formic acid, $R°(H^+)= -5.95$. This means that in 98.3 wt.% formic acid the activity of a concentration equal to 1 mol L^{-1} of H^+ is largely increased vs. pure water ($\Gamma_t(H^+)_{H_2O \rightarrow HCOOH} = 10^{-5.95}$).The diagram also shows that till about 50 wt.% of formic acid, the basicity of water molecules limits the acidity scale ($R°(H^+) \approx 0$). For HCOOH 98.3 wt.% the whole acidity scale is in the super acid medium ($R(H^+)<0$). So even a 1 mol L^{-1} of the strong base formate gives an acidity level higher than 1 mol L^{-1} of H^+ in pure water. This diagram also shows that as soon as formic acid percentage is over 5% by weight (≈ 1 mol L^{-1}) the medium is much more dissociated than pure water ($[H^+] = [HCOO^-] \approx 0.05$ mol L^{-1}) till about 80 wt.% (HCOOH 20 mol L^{-1}). For pure formic acid (98.3% by wt.) the auto dissociation is still appreciable, equal to 0.03-0.04 mol L^{-1}.

4. Conclusions

The autoprotolysis constant of formic acid-water mixtures have been determined by potentiometric titrations of a strong acid by a strong base in a series of mixtures. Fitting of experimental curves with calculated ones allowed an accurate determination of pK_{HS} values giving the amplitude of the acidity scales. The obtained values shows that an increase of formic acid concentration in water leads to more dissociated media than pure water. The pK_{HS} value varies from 3.45 to 5 (HCOOH 4.6 wt.% to 98.3 wt.%) with a minimum value of 2.3 around 50 wt.%. In the range HCOOH 4 mol L^{-1} (17.7 wt.%) to 22 mol L^{-1} (84.6 wt.%) the ionic strength is about 0.03-0.07.

A correlation between acidity scales of formic acid/water mixtures and the acidity scale of pure water has also been achieved by determination of the redox function of Strehlow in each medium. This correlation shows that the acidity level in acidic media is limited by the basicity of water molecules from 0 to 50 wt.% formic acid. For high concentrations of formic acid (>80% by weight), the whole acidity scale is in the superacid part of the generalized acidity scale pH_{H2O}. The diagram also shows that formic acid/water mixtures are relatively dissociated media. This would explain problems encountered in formic acid regeneration from formate by electromembrane process [27]. On the contrary this dissociation is favourable for implementation of direct formic acid fuel cells.

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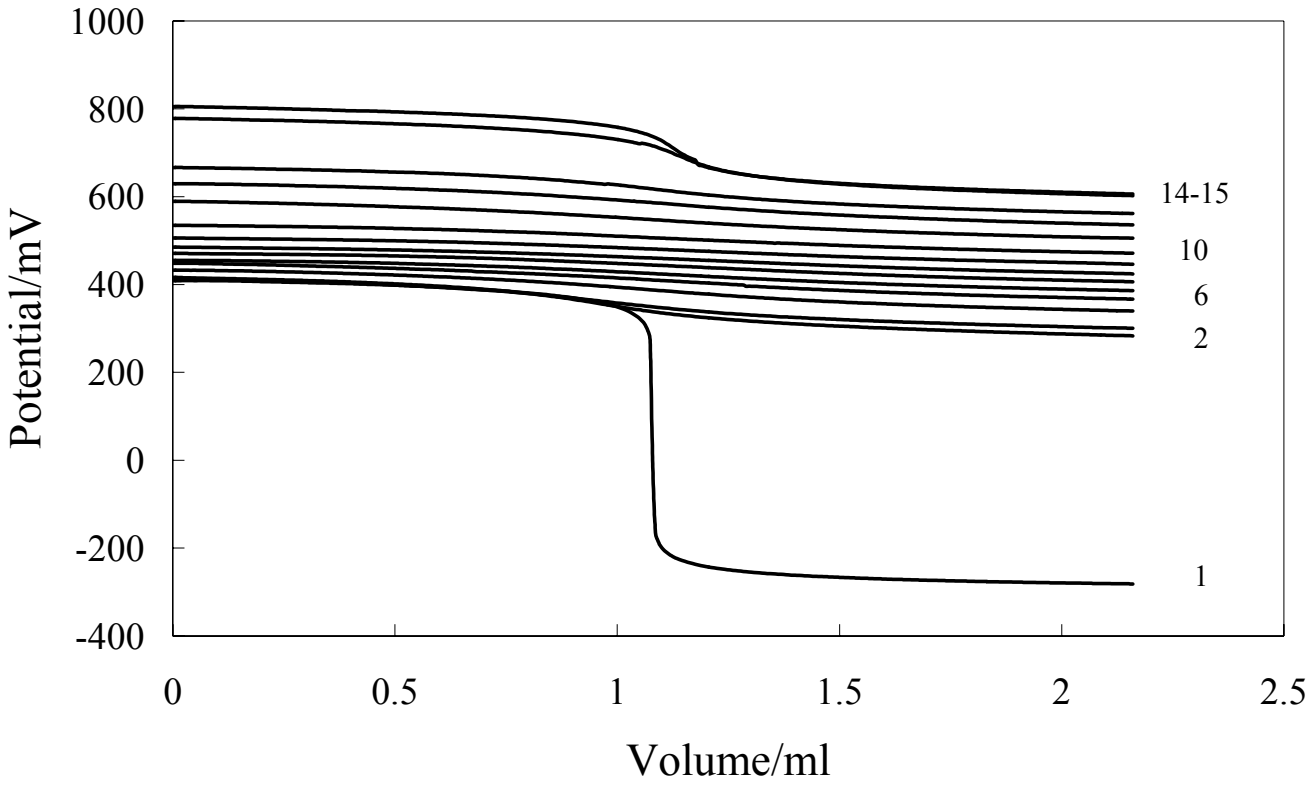
FIGURE 1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200
0
-200
-400
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2
2.5
Volume/ml
14-15
10
6
2
1

FIGURE 2

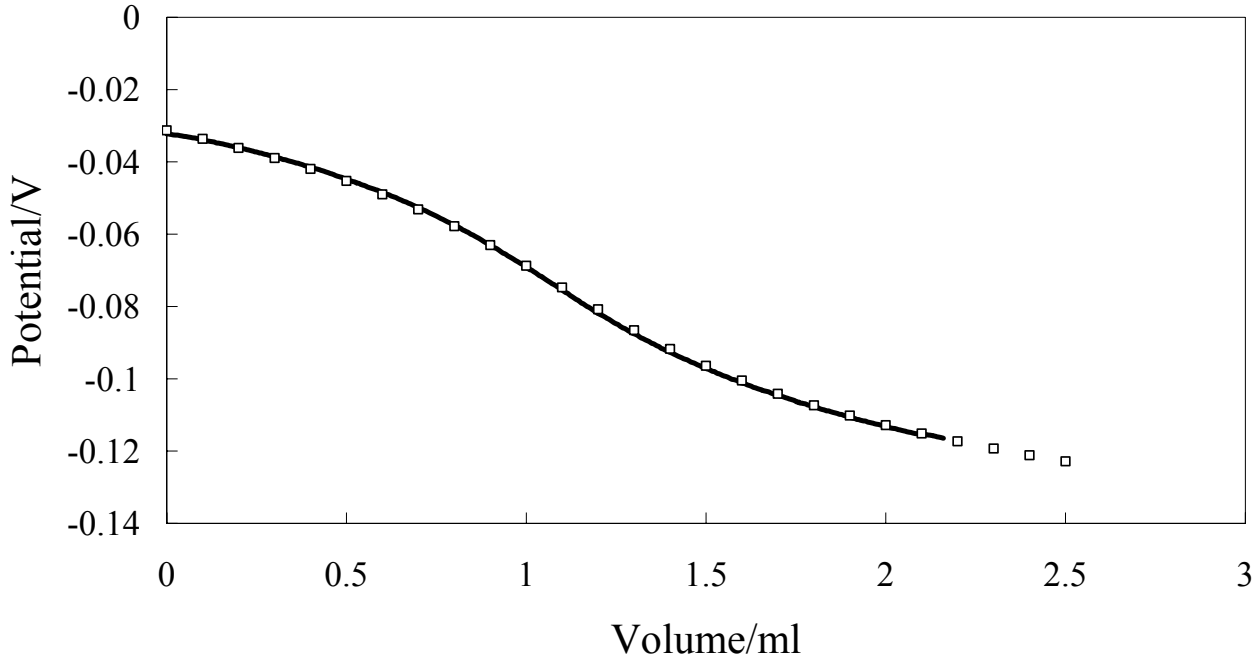


FIGURE 3

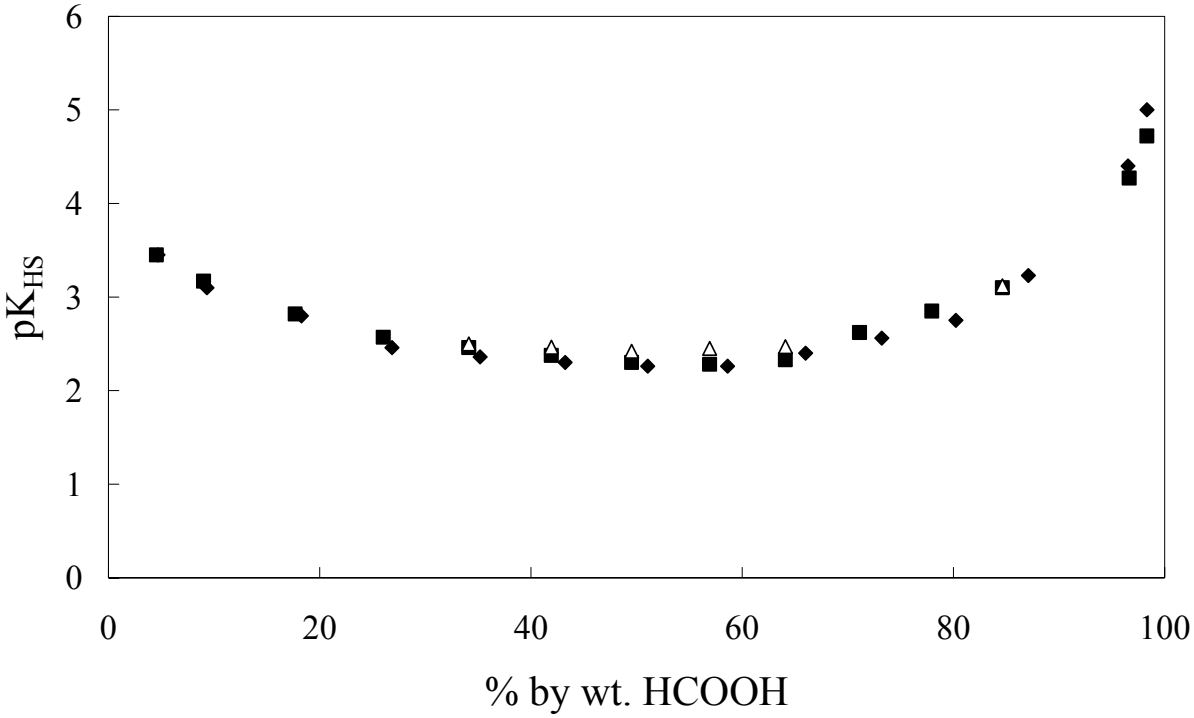
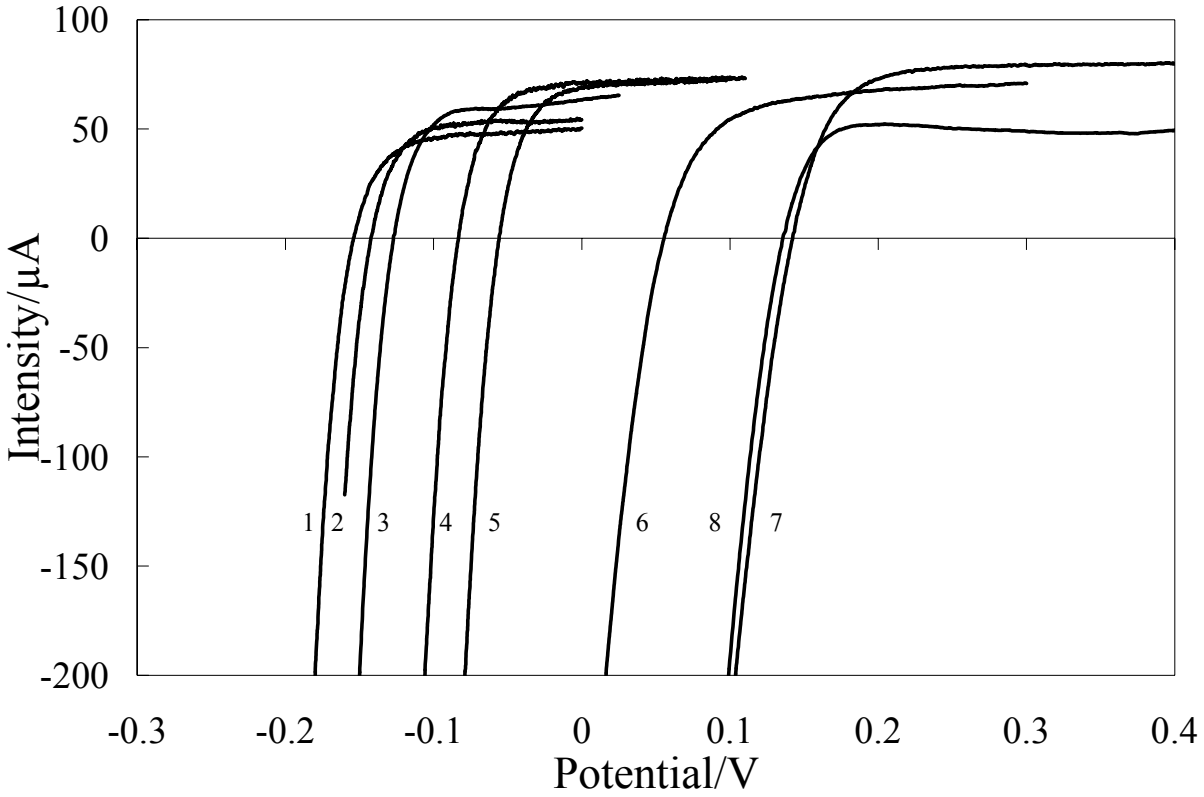


FIGURE 4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-0.2
-0.1
0
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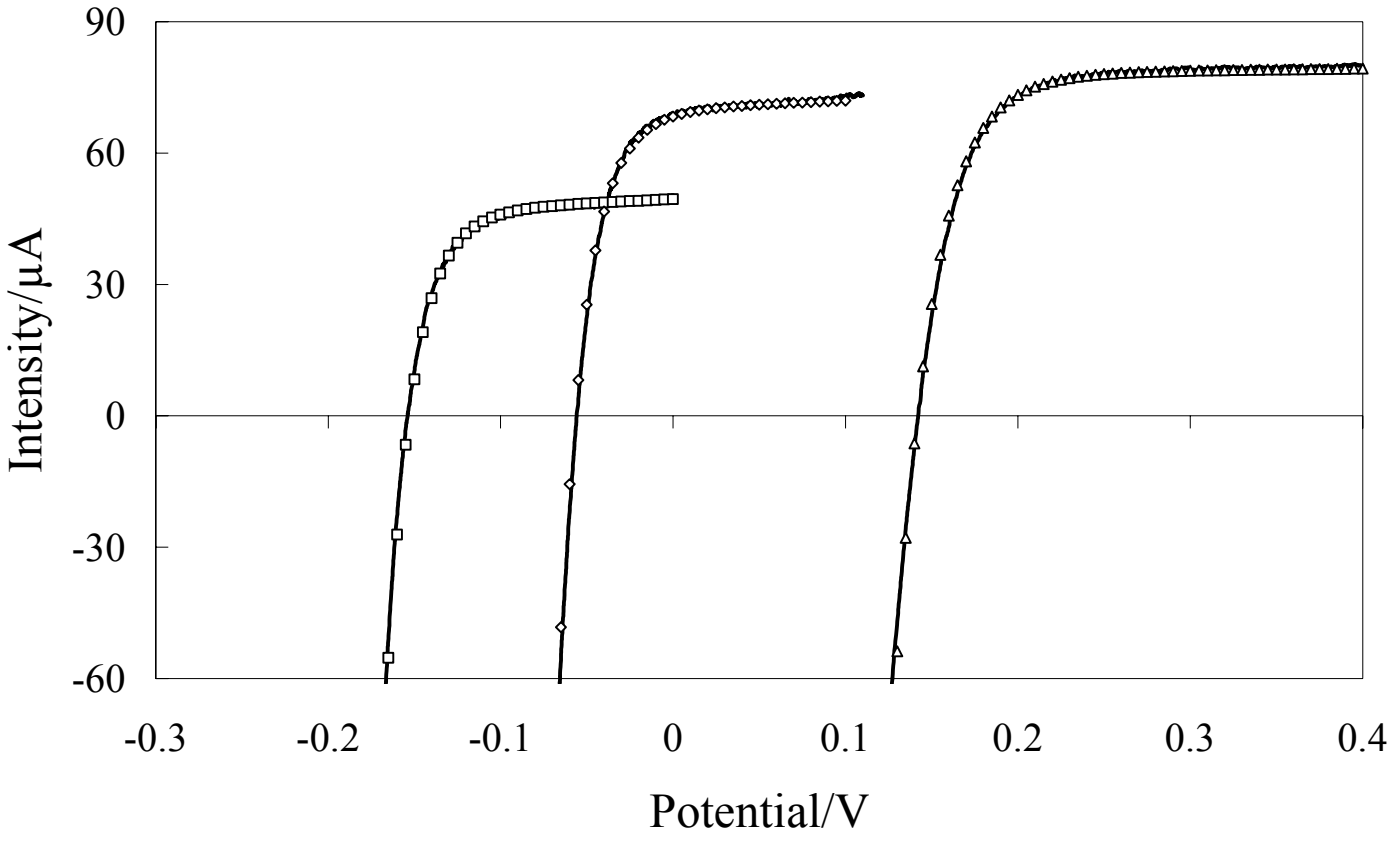
0.2
0.3
0.4
Potential/V
1
2
3
4
5
6
8
7

FIGURE 5



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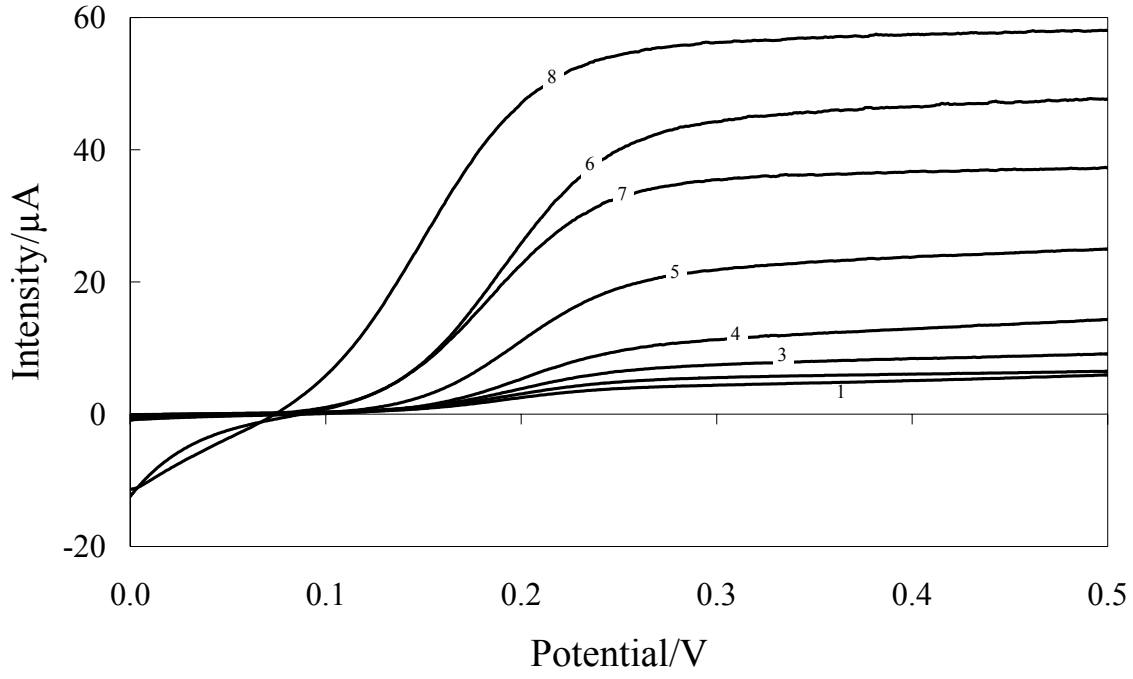

FIGURE 7

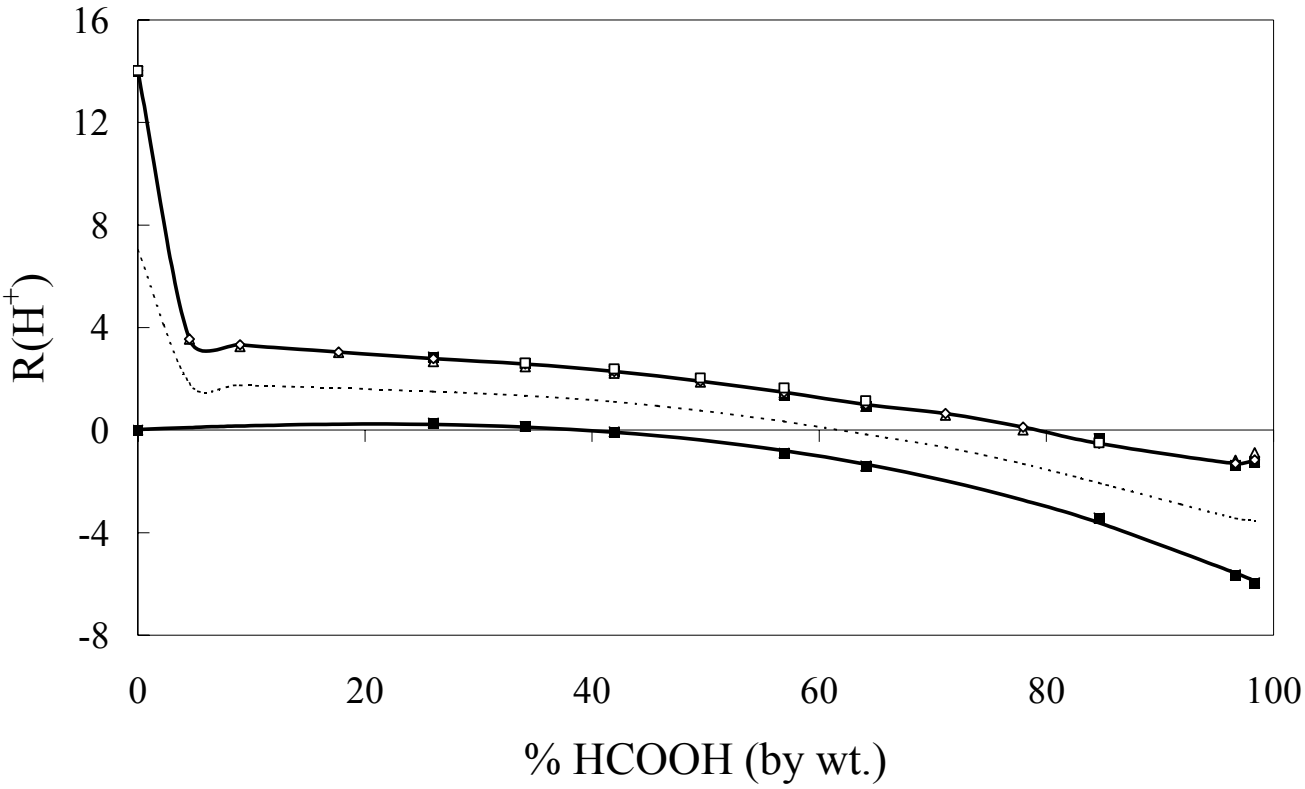

FIGURE LEGENDS

Figure 1
Titration curves of ≈ 0.2 M $HClO_4$ by a 5 M strong base (NaOH or NaHCOO) in formic acid/water mixtures as solvent. Formic acid percentages (by wt.) are: (1) 0%, (2) 4.6%, (3) 9.0%, (4) 17.7%, (5) 26.0%, (6) 34.1%, (7) 41.9%, (8) 49.5%, (9) 56.9%, (10) 64.1%, (11) 71.1%, (12) 77.9%, (13) 84.6%, (14) 96.6%, (15) 98.3%.

Figure 2
Experimental curve for titration of 0.28 M $HClO_4$ by 5 M NaHCOO in formic acid/water 71.1/28.9 wt.%. (□: calculated curve).

Figure 3
Experimental values of autoprotolysis constant pK_{HS} for formic acid/water mixtures. ◆1st series of measures, ■ 2nd series, △3rd series (the point for pure water, pK_{HS}=14, is omitted).

Figure 4
Current-potential curves of the H^+/H_2 electrochemical system for several concentrations of formic acid in water: (1) 6M, (2) 8M, (3) 10M, (4) 14M, (5) 16M, (6) 22M, (7) 25.7M, (8) 26.2M. The working electrode is a rotating platinized platinum one (3.14 mm^2 area, 1000 rpm). All scans are recorded at 1 mVs^{-1}. Potentials are given vs. $Ag/AgCl/KCl_{sat.}$ in corresponding media. The solution is hydrogen saturated and contains $HClO_4$ 1M.

Figure 5
Experimental and calculated current-potential curves for H^+/H_2 electrochemical system.
Continuous lines: experimental curves. Calculated points for HCOOH: □ 6M, ◇ 16M, △ 25.7M.

Figure 6
Current-potential curves for oxidation of ferrocene in H_2O/HCOOH mixtures. HCOOH: (1) 6M; (2) 8M; (3) 10M; (4) 14M; (5) 16M; (6) 22M; (7) 25.2M; (8) 26.2M. Potentials are vs. $Ag/AgCl/KCl_{sat}$ reference electrode. Ferrocene 0.0043 mol L^{-1} is introduced in each solution containing $HClO_4$ 0.25M (only a part is soluble).

Figure 7
Water-formic acid mixing diagram showing variations of the acidity level and pK_{HS} values vs. the generalized acidity scale $R(H^+)$.
■, △, ◇and □ are experimental values. Continuous lines are calculated by polynomial regression from experimental values. Dotted line is the acidity neutrality.

TABLE 1

HCOOH		1st series		2nd series		3rd series	
mol L^{-1}	wt.%	slope (V)	pK_{HS}	slope (V)	pK_{HS}	slope (V)	pK_{HS}
0	0.0	0.0554	14	0.0546	14		
1	4.6	0.0577	3.45	0.059	3.45		
2	9.0	0.059	3.1	0.0585	3.17		
4	17.7	0.0572	2.8	0.0578	2.82		
6	26.0	0.0586	2.46	0.0589	2.57		
8	34.1	0.0584	2.36	0.0578	2.46	0.0599	2.5
10	41.9	0.0576	2.3	0.0584	2.375	0.0586	2.465
12	49.5	0.0579	2.26	0.0579	2.3	0.0582	2.42
14	56.9	0.059	2.26	0.0568	2.28	0.0587	2.45
16	64.1	0.0574	2.4	0.0589	2.33	0.0586	2.47
18	71.1	0.0563	2.56	0.0586	2.62		
20	77.9	0.0591	2.75	0.058	2.85		
22	84.6	0.0564	3.23	0.0577	3.1	0.0583	3.12
25.7	96.6	0.0566	4.4	0.0575	4.27		
26.2	98.3	0.059	5	0.0572	4.72		

TABLE 2

HCOOH		$k°/k_D$	E° vs. Ag/AgCl, KCl_{sat}
mol L^{-1}	wt.%		V
6	26.0	0.4	-0.223
8	34.1	0.7	-0.211
10	41.9	0.7	-0.194
14	56.9	0.7	-0.146
16	64.1	0.6	-0.117
22	84.6	0.1	-0.008
25.7	96.6	0.55	0.112
26.2	98.3	0.4	0.098

TABLE 3

HCOOH		I_{Fec}	$E_{1/2}$
mol L^{-1}	wt.%	µA	V
6	26.0	2.8	0.193
8	34.1	4.6	0.197
10	41.9	5.8	0.202
14	56.9	8.5	0.202
16	64.1	19.8	0.202
22	84.6	43	0.193
25.7	96.6	36	0.185
26.2	98.3	56	0.153

TABLE 4

HCOOH		Potential (V) vs. $Ag/AgCl/KCl_{sat}$		Potential (V) vs. Fec/Fec^{+}	$R°(H^{+})$
mol L^{-1}	wt.%	$E°[H^{+}/H_2]$	E° [ferrocene]	$E° [H^{+}/H_2]$	
6	26.0	-0.223	0.193	-0.416	0.28
8	34.1	-0.211	0.197	-0.408	0.14
10	41.9	-0.194	0.202	-0.396	-0.07
14	56.9	-0.146	0.202	-0.348	-0.90
16	64.1	-0.117	0.202	-0.319	-1.40
22	84.6	-0.008	0.193	-0.201	-3.43
25.7	96.6	0.112	0.185	-0.073	-5.64
26.2	98.3	0.098	0.153	-0.055	-5.95

TABLE HEADINGS

Table 1
pK_{HS} values of formic acid/water mixtures as solvents
(for three series of titration).

Table 2
Determination of standard potential E° of H^+/H_2 system in water/formic acid mixtures. Potentials are referred to $Ag/AgCl/KCl_{sat}$ in each media, computations have been done for $\alpha=\beta=0.5$, $I_{Ox}>>I_R$, $2.3RT/2F=0.03$.

Table 3
Values of the half-wave potentials $E_{1/2}$ for ferrocene oxidation in formic acid-water mixtures. Potentials are referred to $Ag/AgCl/KCl_{sat}$.

Table 4
Values of the redox function $R°(H^+)$ in formic acid-water mixtures.
(calculation with $2.3RT/F=0.058V$)