Transition Between Molten-Salt and Solvated-Ion States of Proton Hydrates: Comparative Double-Layer and Electrode-Kinetic Behaviour at Hg and Au Interfaces

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Z. Naturforsch. 46a, 160–173 (1991); received June 5, 1990

Dedicated to Dr. K. Heinzinger on the occasion of his 60th birthday

The question of the structure of the electrical double-layer at electrodes in contact with electrolyte solutions has several aspects in common with the long and short-range structure of electrolyte solutions. Measurements of the capacitance of the double-layer have traditionally provided information on this question for the case of dilute electrolyte solutions.

With proton hydrates from H$_3$O$^+$ through H$_2$O$_2^+$ to 1 M aqueous H$^+$ solution made by stoichiometric addition of water to the acid CF$_3$SO$_3$H, the transition between "molten-salt" (H$_3$O$^+$ CF$_3$SO$_3$) above 307 K to "dilute-solution" behaviour of the interphasial double-layer at Hg and Au electrodes can be investigated. The H$_2$O$^+$ CF$_3$SO$_3$ is a highly conducting molten salt above 307 K. The results indicate that the double-layer capacitance at potentials negative to the RHE, both at Hg and Au, in the H$_2$O$^+$ molten salt has values surprisingly similar to that in 1 M aq. H$^+$ solution. Intermediate states of hydration of the proton (H$_5$O$_2^+$, H$_7$O$_3^+$, H$_9$O$_5^+$) have higher values, especially at Au. However, the capacitance behaviour is quite different from that observed in high-temperature, alkali-metal molten salts at Pb.

Models are proposed for the structures of the double-layers in these proton-hydrate systems, and the problem of accounting for a "normal" value (ca. 18 μF cm$^{-2}$) of capacitance at Hg in the H$_3$O$^+$ melt is examined by means of some model calculations.

Comparative electrode-kinetic measurements on proton discharge add further information on the behaviour of the proton hydrates.

Introduction

The short- and long-range structure of the electrical double-layer at electrode interfaces bears several similarities to that in solutions of electrolytes [1]. At the interface of electrodes there is a nearest-neighbour solvation layer of water molecules oriented, as at ions, to an extent determined by the charge-density, q, at the interface [2–4] and the corresponding local field. Additionally, there is a layer of electrostatically bound anions or cations [5] (analogous to ion pairing in electrolytes) depending on the sign of q; in the case of anions, the adsorption is often chemisorptive with partial charge-transfer between the ad-ion and the electrode metal [5–7]. Conjugate to the adion layer (Helmholtz planes [5]) is a diffuse ionic atmosphere [7] as with 3-dimensional distributions of ions in electrolyte solutions.

The Gibbs energy of hydration or solvation is one of the principal factors determining the extent to which chemisorption of ions takes place with partial charge-transfer [6, 8, 9] at an electrode; it also determines [10, 11], in part, but in a most important way, the activation energy for ion discharge associated with the coupled process of desolvation of the ion.

Extensive work is to be found in the literature [12–14] on both the problem of structure of electrolyte solutions, especially including that of the solvents themselves (in the case of H$_2$O and CH$_3$OH), and that of interfaces with liquids and electrolyte solutions. Some of this work was informative but empirical in nature [13]. Major improvements have been made in recent years towards in ab initio representation of the structures of liquids [16], ionic solutions [12] and liquid/solid interfaces [15] especially in the molecular dynamics calculations of Heinzinger and his colleagues, as referenced incompletely above. For electrochemistry and solution chemistry, his MD calculations of the positional and orientational distributions of hydrating H$_2$O molecules in the first coordination shells of ions of various charge densities, his evaluations of

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radial distributions for the structure of water and his treatment of the distribution of liquid-phase molecules at/near a wall, have been of particular value.

The proton has been recognized as playing a major role in chemistry and electrochemistry. In particular, the state of the hydrated proton in solution has attached special interest not only from the point of view of electrochemistry but in relation to the physical chemistry of acidity and conductance of acid solutions. Elsewhere this question has been considered [17, 18] and reviewed [19, 20] with regard to the existence of H$_3$O$^+$ itself and characterization of higher states of hydration [21] of H$^+$. Well defined states of hydration and solvation of the proton have also been observed in the vapour phase, and their speciations and stabilities determined, mainly by mass-spectrometry [32].

**Purpose and Scope of the Work**

The purpose of the present work is to examine the progression of the structure of the interfaces between Hg, and comparatively at Au, with a series of states of the hydrated proton that can be experimentally realized between the stoichiometry H$_3$O$^+$, through time-average stoichiometries H$_3$O$_2^+$, H$_3$O$_3^+$, H$_3$O$_4^+$ (cf. [21]) to that corresponding to H$^+$ (aq.), i.e. in dilute aqueous solution. The measurements involve determinations of the interfacial capacitance of Hg and Au electrodes, over a range of potentials, in contact with the melt H$_3$O$^+$·CF$_3$SO$_3$ where the state of H$^+$ as the H$_3$0$^+$ ion can be compared with that of solutions of other states of the hydrated proton up to H$^+$ (aq.) in dilute solution. This provides the opportunity, amongst other things, of comparing the interfacial capacitance of a molten salt at Hg and Au with that of a dilute solution and of intermediate hydrate states of the proton. The double-layer capacitance behaviour at Hg and Au in the low-temperature H$_3$O$^+$ melt can also be compared with that at a Pb electrode in molten NaCl/KCl melts studied at elevated temperatures by Ushke et al. [23].

At Au, these experiments for various CF$_3$SO$_3$H/H$_2$O compositions, enable the interfacial capacitance to be evaluated both at potentials positive to the RHE just prior to Au surface oxidation, and at negative potentials, in the cathodic H$_2$ evolution region. This enables the state of the interface at which proton transfer occurs to be characterized from a “molten-salt” configuration [22] to a regular Stern-Grahame configuration [5, 7] in excess water.

Corresponding kinetic experiments on proton discharge enable the exchange current-densities, $i_0$, the heats of activation $\Delta H^*$ (corrected for variation of the reference electrode potential with temperature from non-isothermal cell measurements) and, in particular, the variation of the Tafel slope, $b$, with temperature (cf. [24, 25]) to be determined, thus adding some further data for new systems with regard to temperature dependence of the transfer coefficient $\alpha$ or the barrier symmetry factor, $\beta$ (cf. [26]).

In the present paper we examine how the state of hydration of the proton and its conjugate anion, CF$_3$SO$_3$-, in trifluoromethane sulphonic acid solutions and in the “room-temperature” melt [21], H$_3$O$^+$·CF$_3$SO$_3^-$, affects the interfacial capacitance behaviour of mercury and gold electrodes and the kinetics of proton discharge at this metal. Previously, we demonstrated [22] that cathodic H$_2$ evolution could be studied from the H$_3$O$^+$·CF$_3$SO$_3^-$ melt and determined the enthalpic ($\beta_H$) and entropic ($T\beta_S$) components of the barrier symmetry factor ($\beta = \beta_H + T\beta_S$, cf. [24–26]) for this process at the Hg electrode in aqueous and methanolic solutions where the simple proton discharge event is rate-controlling.
The results obtained in the present work allow the transition between "molten-salt" to "ionic-solution" behaviour to be investigated, both kinetically and with respect to the double-layer capacitance behaviour at metal/molten H$_3$O$^+$ salt and metal/proton-hydrate interfaces.

**Experimental**

Methods: The interfacial capacitance behaviour of liquid Hg over a range of potentials and at polycrystalline Au electrodes at potentials both positive and negative to the RHE in the same medium was determined in the H$_3$O$^+$.CF$_3$SO$_3^-$ melt and in the other liquid proton hydrate media through to 1 M aqueous solutions of CF$_3$SO$_3$H (see below) as a function of potential on the positive side by cyclic-voltammetry and from a small-amplitude (7 mV) linear potential sweep at 35 mV s$^{-1}$ superimposed on a series of potential steps of 50 mV. The response currents gave the required interfacial capacitance behaviour over the potential sweeps at the controlled potentials of the sequential steps.

The instrumental arrangement consisted of an Hokuto Denko potentiostat commanded by a PAR function generator. This system was also employed to record point-by-point current vs. potential relations for cathodic H$_2$ evolution at Hg and Au, using an on-line minicomputer. This procedure, as used previously [27], ensured very reproducible kinetic results.

At potentials negative to the RHE, the capacitance was determined by means of a.c. impedance and potential-relaxation methods. At Hg, the a.c. impedance behaviour is excellently represented by virtually perfect semicircles in the complex-plane plots of the real ($Z'$) vs. the imaginary ($Z''$) components of the impedance vector. There is no anomalous dispersion corresponding to depression of the centre of the semicircle below the $Z'$ axis as arises at some solid electrodes. The C values can therefore be reliably evaluated.

Technique and Apparatus: All experiments were performed in a thermostated all-glass, 3-compartment cell, using high-purification techniques as described in earlier papers [28, 29].

Electrodes: a) Aldrich Gold Label high-purity Hg was used as a recumbent Hg electrode formed in a glass cup connected to a 1 mm Pyrex capillary joined to an electrical contact and a micrometer syringe. The capillary and cup had been previously silanized to prevent creep of electrolyte below the meniscus, as in other works in the literature. This procedure led to excellently reproducible results. The silanization procedure was repeated, as necessary, at various intervals.

b) Polycrystalline 99.99% pure Au wires from Johnson Matthey were used in the solid-electrode work, with the Au being sealed into soft-glass electrode holders with a spot-welded Ag wire contact to the external circuit. After washing in acetone and pyrodistilled water [29], the Au electrodes were cycled several times in the acid solution at 25 mV s$^{-1}$ between 0.05 and 1.5 V, RHE, to establish an electrochemically clean and reproducible surface.

An H$_2$/Pt or β-PdH electrode in the same solution as the Hg or Au electrodes was used as the reference electrode.

Electrolytes and Solutions: H$_3$O$^+$.CF$_3$SO$_3^-$ was prepared from redistilled CF$_3$SO$_3$H followed by treatment with a stoichiometric mole of H$_2$O. The resulting acid salt, H$_3$O$^+$.CF$_3$SO$_3^-$ (see Results Section), was then distilled in vacuo and collected in glass ampoules which were then sealed until used in the electrochemical interfacial capacitance and H$_2$-kinetic experiments. The acid salt has a m.p. of 307 K and gave a "good quality" cyclic-voltammogram at Au without any indications of effects of impurities in...
the melt or on the Au surface (cf. [29] and [30]); it also
gave the 3-peak solid-state proton n.m.r. spectrum
(Fig. 1) characteristic of the structure H₃O⁺ · CF₃SO₃⁻
rather than the monohydrate CF₃SO₃H · H₂O (cf.
[31]).

Aqueous solutions of redistilled CF₃SO₃H were
made up accurately in pyrodistilled water [29] to give
also nominal compositions corresponding to the pro-
ton hydrate species H₅O₂⁻, H₇O₃⁻ and H₉O₄⁺ (cf. [21]
and [32]), and to 1 M aq. solution.

Results and Discussion

1. Introduction

Results will be presented for Hg electrodes at 298 K
and compared, in a later section, with those obtained
under similar conditions at the non-electrocatalytic
solid electrode, Au. Thus, in many ways, Au, as a
solid metal, provides a basis for comparison with the
liquid metal (298 K) Hg since both have filled 4f and
5d electron shells, and 1 and 2 electrons, respectively,
in the 6s valence electron sub-shell. Neither electrode
exhibits any significant H chemisorption in cathodic
H₂ evolution, indicating a rate-controlling proton-
discharge step in that process (cf. [33] and [34]).

2. Capacitance Behaviour at Hg in the Proton Hydrates

It is well known (e.g. [5]) that in sufficiently strong
electrolyte solutions, as is the case there, the measured
double-layer capacitance, C, represents, to a good
approximation, the compact double-layer capacitance,
C_c, since the diffuse-layer capacitance, C_d, in the re-
ciprocal relation C⁻¹ = C_c⁻¹ + C_d⁻¹ is ≫ C_c. Hence C
provides values of the compact-layer capacitance
which gives information on the short-range geometry
and structure of the interphase. In the species of sys-
tems of proton hydrates studied in the present work,
this structure will change from that corresponding to
a distribution of H₃O⁺ cations and CF₃SO₃⁻ anions
with supposedly no free water present, through struc-
tures involving hydrated H₂O⁺ and CF₃SO₃⁻ ions
with varying quantities of associated or free
water.

Figure 2 shows that for dilute aqueous solutions of
CF₃SO₃H (fully dissociated as H⁺ aq. + CF₃SO₃⁻ aq.)
the interfacial capacitance for Hg is of the expected

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Fig. 2. Double-layer capacitance vs. potential profiles for Hg at 313 K in 3 × 10⁻², 10⁻³, and 10⁻² M aq. CF₃SO₃H solutions (strongly dis-
sociated to H₃O⁺ + CF₃SO₃⁻ ions).
The capacitance behaviour at Hg, as a function of potential, for four proton hydrate trifluoromethane sulphonates, H$_3$O$^+$ to H$_9$O$_4^+$, is shown in Fig. 3 and for 1 M aq. solution in Fig. 4 for comparison. The behaviour for the latter solution does not, of course, exhibit a minimum (cf. Fig. 2) since $C_q \gg C_c$ for such concentrations.

Note that if these curves of Figs. 3 and 4 were to be compared as a function of potential vs. SHE they would be appreciably displaced laterally on the potential scale due to the large proton activity (or mean acid activity) differences from H$_3$O$^+$ in the melt, through the proton hydrates, to approximately unit activity in the 1 M aq. acid solution.

A comparative view of the capacitance behaviour at Hg for the five states of the hydrated proton is shown in Fig. 5. Here it is seen that the main differences of significance arise at potentials negative to the p.z.c. This is as expected since, at such potentials, the proton hydrate cations predominantly populate the compact layer. The lowest capacity arises with the H$_2$O$^+$ molten salt, where the distance of closest approach to the Hg surface for negative values of $q$ will be determined by the radius of H$_3$O$^+$ while, for higher hydrates, this factor will be larger, tending to give rise to lower compact layer capacitances owing to a thicker compact layer. The effect is, however, evidently outweighed by a smaller dielectric constant due to absence of free H$_2$O molecules.

Formally, $C_c = \varepsilon_0 \varepsilon_c / 4 \pi d$, where $\varepsilon_c$ is the dielectric constant of the compact layer region, $\varepsilon_0$ the permittivity of vacuum and $d$ the effective dielectric thickness of the compact region of the interphase. With increasing extent of hydration of H$^+$ in the interphase, both $\varepsilon_c$ and $d$ will tend to increase, so $C_c$ can either increase or decrease with changing degree of hydration of H$^+$.

The variation of $C_c$ for Hg with the increase of hydration, expressed as different hydrate species from H$_3$O$^+$ through H$_9$O$_4^+$ to 1 M aq. H$^+$, is shown in Figs. 6a, b, c for the three cathodic potentials from which it is seen that, in fact, there is a significant maximum and minimum in $C_c$ as a function of the proton speciation. These variations of $C_c$ by about 5 to 8 $\mu$F cm$^{-2}$ are well outside the possible error, $\Delta$, of measurement of $C_c$ which is ca. $\Delta C_c = 0.5$ $\mu$F cm$^{-2}$ except at extremes of the "d.c." polarization potentials. The variations of $C_c$ are therefore experimentally significant for the dependence of structure of the double-layer at Hg on extent of proton hydration and water dipole orientation [2, 3].

It is to be noted from Fig. 6 that the maxima or minima in the dependence of $C_c$ on speciation do depend significantly on the potential; this must be
3. Capacitance Behaviour at Au in the Proton Hydrates

At this point, it is convenient to compare the above results with those for Au, as a function of proton hydrate speciation.

The capacitance behaviour at Au in the various proton-hydrate solutions is shown as a function of potential in Figs. 7a–d for the potential range 0 to 1.8 or 2.0 V vs. RHE, positive to the RHE potential in the same respective solutions.

Previous work at Au in aq. H₂SO₄ and HClO₄ showed [35] that regions of potential-dependent capacitance precede the initial stage of surface oxidation by 0.8 V or more and hence represent a stage of “pre-oxidation” of the Au surface by partial discharge of the anion. Similar effects are found for the behaviour in the CF₃SO₃⁻ proton hydrate systems. Thus, from cyclic-voltammograms taken at sensitive potentials, the capacitance of Au tends to become populated with CF₃SO₃⁻ anions (for the special situation in the H₃O⁺ melt, see the double-layer structure diagram, Fig. 12 later).

attributed presumably to the potential-dependence both of εₓ and d in the the equation for Cₓ.

At potentials positive to the p.z.c. at Hg, all the Cₓ vs. E curves are quite similar (Fig. 5) (except at extreme positive potentials where preoxidation of Hg tends to occur due to Hg₂(CF₃SO₃)₂ formation). This is understandable since the inner region of the compact layer then tends to become populated with CF₃SO₃⁻ anions (for the special situation in the H₃O⁺ melt, see the double-layer structure diagram, Fig. 12 later).

Fig. 5. Comparative plot of the capacitance behaviour of the Hg-pool electrode in the various proton-hydrate/CF₃SO₃⁻ systems.

Fig. 6. Capacitance values for the Hg-pool electrode as a function of proton-hydrate speciation at the 3 cathodic over-potentials −0.3 V, −0.4 V (vs. SHE) and −0.7 V (vs. RHE).
Fig. 7. Capacitance vs. potential profiles for the Au electrode in the proton hydrate systems as determined by small-amplitude cyclic linear sweeps on successive potential steps into the region of commencement of surface oxidation: a) H$_2$O$^+$; b) H$_2$O$_2$; c) H$_3$O$_x$ and d) 1.0 M aq. solution of CF$_3$SO$_4$H.
current scales, it is possible to estimate the extent of charge-transfer, \( \delta q \), associated with the pseudocapacitance due to anion chemisorption in the potential range +0.15 to 1.27 V, RHE for the case of the \( \text{H}_3\text{O}^+ \cdot \text{CF}_3\text{SO}_3^- \) melt; from the cathodic and anodic sweeps, the values of \( \delta q \) are found to be 23 and 23 \( \mu \text{C cm}^{-2} \), taking the three trigonal O atoms in the \( \text{CF}_3\text{SO}_3^- \) as occupying 3 Au sites (cf. [35] for \( \text{HSO}_4^- \) and \( \text{ClO}_4^- \)). From these data, it can be concluded that there must be an appreciable degree of charge transfer of at last 0.5 e per anion, allowing for the possibility that some \( \text{H}_3\text{O}^+ \) ions also populate the interface at these positive potentials, i.e. the coverage fraction by \( \text{CF}_3\text{SO}_3^- \) may be somewhat less than unity, especially in the \( \text{H}_2\text{O}^+ \) melt.

At other degrees of hydration of \( \text{H}^+ \), it is more difficult to distinguish the adsorption pseudocapacitance contribution due to anion chemisorption from the background electrostatic interfacial capacitance, but approximate values of \( \delta q \) of 20 to 25 \( \mu \text{C cm}^{-2} \) may again be estimated.

For potentials on the cathodic side of the \( \text{H}_2 \) reversible potential at Au, Fig. 8 shows the capacitance behaviour as a function of cathodic \( \text{H}_2 \) overpotential from \(-0.1 \) to \(-0.35 \) V, determined by means of a.c. impedance and potential-relaxation measurements [27, 34, 36]. These two methods give results in quite good agreement, mostly to within \( 1 \sim 2 \mu \text{F cm}^{-2} \).

The dependence of the capacitance at Au at \( \text{H}_2 \) overpotentials of \(-0.1 \) to \(-0.3 \) V on proton-hydrate speciation is shown in Figure 9. Here it is clear that a) a single maximum arises between the states \( \text{H}_5\text{O}_2^- \) and \( \text{H}_7\text{O}_2^- \) and b) that the \( C_e \) value for the \( \text{H}_3\text{O}^+ \cdot \text{CF}_3\text{SO}_3^- \) melt is quite close to that for the 1 M aq. \( \text{H}_3\text{O}^+ \) solution, the values being ca. 25 and \( 24 \mu \text{F cm}^{-2} \), respectively. The data points for potentials in the \( \text{H}_2 \) evolution region were evaluated by a.c. impedance at various potentiostatically held polarization potentials and from analysis of potential relaxation transients after polarization [27, 36].

At Au it is evident that the maximum value of \( C_e \) (about \( 48 \mu \text{F cm}^{-2} \) between \( \text{H}_5\text{O}_2^- \) and \( \text{H}_7\text{O}_2^- \) is about twice the values, 24 and \( 25 \mu \text{F cm}^{-2} \), at the two ends of the curve. This difference is larger than those at Hg (Fig. 6). At Au, the data plotted are for \(-0.1 \) to \(-0.3 \) V vs. RHE while for Hg (Fig. 6) the data were plotted for three potentials \(-0.3, -0.4 \) V vs. SHE and \(-0.7 \) V vs. RHE.

**Comparison of Capacitance Values at Hg and Au in the H\(_3\)O\(^+\) Melt and for 1 M aq. H\(^+\)**

A comparative tabulation of actual values of \( C \) for Hg and Au at potentials negative to the RHE is given in Table 1.

For the data in the \( \text{H}_2 \) evolution potential range (\(-0.1 \) to \(-0.3 \) V RHE), the main point of interest is...
Table 1. Interfacial capacitance values for polycrystalline Au wire and liquid Hg at 313 K in solutions of the proton in various states of hydration.

<table>
<thead>
<tr>
<th>Nominal state of the hydrated proton</th>
<th>Capacitance value/μF cm⁻² *</th>
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<tbody>
<tr>
<td>( \text{H}_3\text{O}^+ )</td>
<td>33.3</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2^+ )</td>
<td>45.6</td>
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<tr>
<td>( \text{H}_2\text{O}_3^+ )</td>
<td>54.3</td>
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<tr>
<td>( \text{H}_2\text{O}_4^+ )</td>
<td>45.8</td>
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<tr>
<th>Electrode potential vs. RHE/V at Au</th>
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<tbody>
<tr>
<td>-0.10</td>
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<tr>
<td>-0.20</td>
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<td>-0.25</td>
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<th>Electrode potential vs. RHE at Hg</th>
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<tr>
<td>-0.5</td>
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<tr>
<td>-0.55</td>
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<tr>
<td>-0.6</td>
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<td>-0.65</td>
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<tr>
<td>-0.7</td>
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<tr>
<td>-0.75</td>
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<td>-0.8</td>
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* Uncertainties in these values are ca. 0.5 μF cm⁻².

that the interfacial capacitance values lie in the range 25 to 33 μF cm⁻² for Au in the \( \text{H}_3\text{O}^+ \) molten salt, quite close to the range of values, 24 to 31 μF cm⁻², found for 1 M aq. solutions (Table 1) where the values for Hg are in the range 16 ~ 20 μF cm⁻². The potentials in the range covered in this Table and Fig. 6 are some 0.5 to 0.7 V negative to the p.z.c. of Au (in dilute solutions), so are probably not influenced by the chemisorption of \( \text{CF}_3\text{SO}_3^- \) indicated from Figs. 7a–d. The surprising result therefore seems to be that the capacitance is determined principally by the contact distance between \( \text{H}_3\text{O}^+ \) and the Au surface, independent of the influence of closely surrounding \( \text{CF}_3\text{SO}_3^- \) anions in the melt or of water molecules in the aqueous solution case (column 6, Table 1), the difference between the data at the same respective potentials being only ca. 10 ~ 15%. However, the changing state of hydration of the proton in going from \( \text{H}_3\text{O}^+ \) to the fully aquated proton, through the intermediate states \( \text{H}_2\text{O}_2^+ \), \( \text{H}_2\text{O}_3^+ \), evidently does have a substantial effect on the capacitance at cathodic overpotentials, with maximum values being exhibited around a degree of hydration corresponding to “\( \text{H}_2\text{O}_3^+ \)” (Fig. 9), with the ratio between the lowest and highest values being about 2, well outside the limits of error and reproducibility in the capacitance values determined by the two methods (Fig. 8). Also, the variations of C with state of hydration of the proton are reasonably consistent for all four cathodic potentials for which data were acquired at Au (Fig. 9); at Hg, the data show some variability with speciation but this is not due to experimental error.

In dilute aqueous medium, values of \( C \) greater than the value of ca. 17 μF cm⁻² found at Hg for potentials negative to the p.z.c., arise at e.g. Ga [37]. Schmickler has treated this matter and shown [38] that values of \( C \) significantly larger than those at Hg can be accounted for in terms of the free electron density in the metal. However, it is difficult to adduce this as the reason for the 48 μF cm⁻² value for Au in ca. \( \text{H}_2\text{O}_3^+ \) medium since lower values at the same metal are found in \( \text{H}_3\text{O}^+ \) medium and 1 M aq. media (Table 1 and Fig. 9). Hence the high \( C \) values for intermediate states of hydration of \( \text{H}^+ \) must be attributed to the specific extent of solvation of the proton coupled with the co-anion concentration. While the above difference for Au must be due to the different states of proton hydration, Table 1 shows that there is, however, a systematically larger series of values of \( C \) at Au than at Hg for respective proton hydrate species. It is this effect that could be caused by the different free electron density at Au than Hg.

We have referred to various proton-hydrate species in discussion of the above results. Apart from \( \text{H}_3\text{O}^+ \) in the \( \text{H}_3\text{O}^+ \cdot \text{CF}_3\text{SO}_3^- \), the stoichiometrics of the hydrates will be time-average ones. That they have some reality in terms of stability is indicated by their observation in vapour-phase experiments in the mass-spectrometer by Knewstubb and Tichner [39], as illustrated in Fig. 10.


The work of Ukshe et al. [23] on double-layer capacitance behaviour at a molten Pb electrode in alkali-halide melts at elevated temperature enables an interesting comparison to be made with the present results on the molten \( \text{H}_3\text{O}^+ \cdot \text{CF}_3\text{SO}_3^- \) salt measured at 313 K. The behaviour observed in the \( \text{H}_3\text{O}^+ \cdot \text{CF}_3\text{SO}_3^- \) melt at Hg or Au is quite contrary to that reported for Pb in the molten alkali-metal salts at high temperature in the above work, where a sharp minimum around the p.z.c. of Pb is observed, reminiscent of the potential-dependence of the diffuse-layer capacitance in dilute aqueous solutions, although there can, of course, be no diffuse-layer in the interphasial region of a molten salt in contact with an electrode but probably rather an oscillatory charge-
distribution over several ionic diameters away from the interface. It was suggested that the distribution of detects in the melt (cf. [23]) could behave analogously to a diffuse-layer, the Debye-Hückel ionic atmosphere giving large diffuse-layer type capacitance values around the p.z.c. However, such values should combine in the usual way with a short-range Helmholtz-layer capacitance giving rise to limits of the rise of the quasi-diffuse-layer capacitance as potentials sufficiently divergent from the p.z.c. are covered. This is not the case for the molten alkali-halides, where $C$ rapidly increases in an exponential or parabolic way, away from the p.z.c., as illustrated in Fig. 11, while the data for Hg and Au show no such minimum (see also Fig. 11).

5. Double-Layer Structure in the Proton Hydrate Media

The transition in configuration of the double-layer which must arise through increasing degrees of hydration of $\text{H}_3\text{O}^+ \cdot \text{CF}_3\text{SO}_3$ is expected to be substantial; it can be qualitatively illustrated in the schematic way shown in Fig. 12. In the melt, at appreciable negative charge densities on the electrode, the charge distribution must approach, locally, that of a triple layer: $\text{M}^+ \cdot \text{H}_3\text{O}^+ \cdot \text{A}^-$. As more water is associated with the proton (it will be preferentially associated with the latter ion since $\text{CF}_3\text{SO}_3$ is a large anion), water of hydration of $\text{H}_3\text{O}^+$ will appear in the inner-layer together with some solvent-shared ion pairs nearby (Fig. 12b); in excess water ($\text{H}^+ \text{aq.}$, Fig. 12c), the normal situation of an outer Helmholtz plane, populated by $\text{H}_3\text{O}^+$, together with an inner layer of...
Fig. 12. Schematic diagrams representing the transition of double-layer structure between molten $\text{H}_3\text{O}^+\cdot\text{CF}_3\text{SO}_3^-$ and dilute aq. solutions of $\text{H}^+$.  

oriented $\text{H}_2\text{O}$ dipoles [2, 3], may be assumed to arise, but note that, statistically, some conversion of inner-layer $\text{H}_2\text{O}$ molecules to $\text{H}_3\text{O}^+$ will be able to occur through the usual proton-hopping mechanism [17, 18]. Since however, the compact layer capacitance at Hg is similar for aqueous acid solutions to those of $\text{NH}_4^+$ and $\text{K}^+$ ions of similar radii, the preferred time-average location of $\text{H}_3\text{O}^+$ is clearly in the outer Helmholtz plane.

The two extreme structures of the double-layer suggested in Fig. 12a and c, represent very different electrostatic situations: limitingly a “triple-layer capacitor”, $-++-$, in Fig. 12a and the usual series combination [5] of a dipole capacitance [2, 3] with an ionic/electronic charge capacitance: $1/C = 1/C_{\text{dipole}} + 1/C_{\text{Helmholtz}}$, in Fig. 12c.

We have mentioned, in Sect. 4, that the capacitance results show a remarkable difference in behaviour from those determined by Ukshe et al. [23] in molten inorganic salts, e.g. NaCl, NaBr, NaI, at a molten lead electrode around 1073–1093 K (Fig. 11) where a relatively sharp minimum arises in $C$ at or near the p.z.c., the minimum values in $C$ being in the range 30 to 75 $\mu$F cm$^{-2}$, depending on the anion of the salt. The present results for the melt $\text{H}_3\text{O}^+\cdot\text{CF}_3\text{SO}_3^-$ show no significant minimum in the whole experimental potential range $-0.3$ V to $1.3$ V RHE at Au or $-0.8$ V to $+0.35$ V RHE at Hg, beyond which positive potentials surface oxidation commences. Of course, the behaviour found by Ukshe et al. [23], although similar to that observed at Hg around the p.z.c. in dilute solutions, cannot arise for the same reasons involving properties of a Gouy-Chapman diffuse layer [5, 7].

In the present examples of the behaviour of proton hydrates at Au, earlier results showed [40] that at potentials positive to the RHE in the same medium, specific adsorption of the anion $\text{CF}_3\text{SO}_3^-$ dominates the capacitance behaviour over the potential region (ca. +0.5 ± 0.1 V, RHE) where the p.z.c. is otherwise expected to arise, so that this may be the reason why no minimum is observed. This may also be due to the much lower temperature than that in the work of Ukshe et al. [23], which will favour anion adsorption, or to H-bonding in the present case of $\text{H}_3\text{O}^+\cdot\text{CF}_3\text{SO}_3^-$. In the media containing further water molecules, up to $\text{H}_3\text{O}^+ + 3\text{H}_2\text{O} (\text{H}_9\text{O}^3_2)$, the interfacial capacitance at the potentials negative to the RHE becomes almost...
doubled. Although the double-layer will then be populated by water-separated ion pairs which increase the distance of the $H_2O^+$ layer from the metal surface, the dielectric constant may be sufficiently increased by the additional water present that the resulting capacitance is substantially larger. Obviously this is determined in a rather inaccessible way by the ratio $\varepsilon/d$, where both $\varepsilon$ and $d$ can be changing. Under the conditions of restricted water content, a free $H_2O$ dipole capacitance [3] in the inner layer is unlikely to be developed (as it is in dilute solutions) owing to the strong solvational binding of $H_2O$ molecules between $H_3O^+$ and $CF_3SO_3^-$ (solvent-separated ion pairs). Also the proton charge can become diffused between the 2, 3 and 4 water molecules of hydration [17, 18] hydrogen bonded to $H_3O^+$. In the extreme of excess water (1M aq. $H^+$), the situation at potentials cathodic to the RHE is presumably represented by conventional models [3, 5].

6. Numerical Values of the Capacitance in the $H_3O^+ \cdot CF_3SO_3^-$ Melt

The numerical values of the capacitance both for the $H_3O^+ \cdot CF_3SO_3^-$ melt at Hg and Au and also for the molten-metal salts of [23] are unexpected high. Thus, one of the most interesting and seemingly surprising results of the present work is the similarity of compact double-layer capacitance values, at potentials negative to the p.z.c. both for Hg and Au, for the two extreme states of hydration of the proton: $H_3O^+$ in the $H_2O^+ \cdot CF_3SO_3^-$ melt and $H^+$ aq. in 1 M aqueous $CF_3SO_3H$ solution, as referred to earlier.

For ordinary dilute aqueous solutions, e.g. at Hg at potentials negative to the p.z.c. where [5] $C_e \approx 18 \mu F cm^{-2}$, the application of simple electrostatics leads from this value of $C_e$ to a physically reasonable value of $\varepsilon$ for the compact layer region. Thus, with units of metres, $C = 1.8 \times 10^{-11} F m^{-2}$, the thickness, $d$, of the compact double-layer taken as its usually assumed value ca. $4.2 \times 10^{-10} m$ (= $r_{H_2O^+} + 2 r_{H_2O}$) and $\varepsilon_0$, the permittivity of free space, taken as $8.85 \times 10^{-12} F m^{-1}$, we find, using the appropriate units,

$$\varepsilon = \frac{d C_e}{\varepsilon_0} \approx 8.5.$$  \hspace{1cm} (1)

This is actually the more or less expected order of the value for $\varepsilon$ in the compact layer at appreciable charge densities where (cf. [3, 41, 42]) significant saturation of the orientational polarization in $\varepsilon$ can arise, giving values substantially less than the bulk, zero-field value, as in hydration shells around ions [43].

The fact that $C_e$ for Hg or Au, at negative electrode charge-densities, is also ca. 16 $\mu F cm^{-2}$ for the $H_3O^+$ melt seems initially a surprising result since there is no dielectric fluid between either the $H_3O^+$ cations or the $CF_3SO_3^-$ anions and the Hg or Au metal surfaces. However, considering the $C$ values for the $H_2O^+$ melt (Table 1) and assuming that the effective charge separation distance, $d$, across the interphase is equal to the radius, 0.138 nm, of the $H_3O^+$ ion, the resulting dielectric constant value would be ca. 3.2. Since, in the $H_2O^+$ melt, free water is absent, the above value seems physically reasonable. For the higher hydrates, the effective interfacial separation of charges across the double-layer would be expected to be significantly larger than that for the $H_3O^+$ melt, e.g. by the diameter, 0.28 nm, of the $H_2O$ molecule, but this will only tend to lower the value of $C$ whereas, experimentally, for $H_2O^+$ and $H_3O^+$ media the capacities at Au are actually about twice that for $H_3O^+$. Bearing in mind, however, the shape and charge-distribution in the $H_2O^+$ ion [17, 19] the actual positive charge delocalized over the three protons could reside preferentially on one side of the trigonal pyramidal molecule ion so that the proton charge-density could come substantially nearer to the electrode surface of the electrode than would be indicated by the overall ionic diameter, but hardly less than the Bohr radius (ca. 0.1 nm) of the $H$ atoms of $H_3O^+$. The electron-overspill effect at negative surface charge-densities would tend to enhance this effect. Although $H_2O^+$ is a fluxional molecule, like $NH_3$, proximity to the negatively charged electrode surface might be expected to lead to preferred orientation of the three protons on the metal side of the $H_2O^+$ ion. This would lead, with $d$ now taken as ca. 0.1 nm, to $C \approx 22 \mu F cm^{-2}$, close to the observed value at Hg (Table 1).

A tentative hypothesis might be that the $H_3O^+ / CF_3SO_3^-$ ion pair polarization in the interphase, analogous to the Maxwell-Wagner effect, gives rise to a high value of $C_c$, fortuitously near that in dilute aqueous solutions but for a completely different reason.

A more quantitative examination of the significance of the $C$ values for the higher proton hydrates at Hg or Au is difficult since as $d$ tends to increase with increasing degree of hydration, $\varepsilon$ will also tend to become larger as the fraction of water molecules...
becoming rotationally freer (cf. [44]) in the interphase increases; thus \( C \) depends sensitively on the ratio \( \varepsilon/d \), and both may be changing as we have remarked earlier.

7. Kinetics of Proton Discharge at Au and Hg

Using the series of proton hydrates, the electrode-kinetics of proton discharge was also evaluated. It may be expected that the kinetics of this process will be dependent on the state of hydration of the proton and on the structure of the double-layer in which the proton source resides. From Tafel polarization relations between current-density \( (i) \) and potential \( (V) \), the log[exchange current-densities, \( i_0 \)], and the Tafel slopes, \( b=dV/d \log i \), were evaluated in the usual way. The dependences of \( \log i_0 \) and \( b \) values for the \( \text{H}_2 \) evolution reaction at Au on speciations of the proton hydrate-CF\(_3\)SO\(_3\) electrolytes are shown in Figure 13.

For both Hg and Au, insignificant coverage of chemisorbed H, electro-deposited from the solvated proton, is observed. Hence, it is usually assumed that the step of proton discharge

\[
e + \text{H}^+ (n\text{H}_2\text{O}) + M (\text{Hg or Au}) \to \text{MH}_{\text{ads}} + n\text{H}_2\text{O} \tag{I}
\]

is rate-determining for the overall reaction of \( \text{H}_2 \) formation which involves, as a second step, either the electrochemical desorption process

\[
e + \text{H}^+ (n\text{H}_2\text{O}) + \text{MH}_{\text{ads}} \to \text{H}_2 + n\text{H}_2\text{O} + M \tag{II}
\]

or the catalytic recombination

\[
2 \text{MH}_{\text{ads}} \to \text{H}_2 + 2M \tag{III}
\]

Thus the kinetic parameters in Fig. 13 will refer to step (I). In considering the sequence of values of \( \log i_0 \), it must be remembered that there is a major increase in concentration from the 1 M \( \text{aq. H}^+ \) solution to the \( \text{H}_3\text{O}^+ \) melt (14 molal).

From experiments at various temperatures at Au, the Tafel \( b \) values at these temperatures can be compared. It is found, surprisingly, that the \( b \) values decrease with temperature, contrary to the expectations from conventional representations of \( b = 2.3 \text{RT}/[\beta_{\text{H}} + \beta_{\text{S}} T] \text{F} \) which always decreases with increasing numerical value of the potential (in the negative direction for a cathodic process). Since the term \( (\beta_{\text{H}} + T\beta_{\text{S}})^2 \) must always be positive, it is clear that (2), based on the relation \( \beta = \beta_{\text{H}} + T\beta_{\text{S}} \), can never account for the direction of change of \( b \) values with temperature for proton transfer at Au from the \( \text{H}_3\text{O}^+ \) melt or the \( \text{H}_5\text{O}_2 \) hydrate.

We have considered whether the observed behaviour could arise on account of a temperature-dependence of the pre-exponential transmission coefficient, \( \kappa \), in reaction kinetics since, formally, an apparent temperature-dependence of \( \beta \) corresponds [26, 45] to a potential-dependence of the entropy of activation, \( \Delta S^+ \), of the process. A potential-dependence of \( \kappa \) could correspond to an apparent potential-depen-

\[
\beta_{\text{H}} \text{ is an enthalpic and } T\beta_{\text{S}} \text{ an entropic component of } \beta, \text{ representing the effect of electrode potential on the Gibbs energy of activation of the proton discharge process. Here, in order to understand the unusual decrease of } b \text{ with } T, \text{ it is necessary to account for a negative value of } d\beta/dT \text{ in the above expression for } b\left(= 2.3 \text{RT}/[\beta_{\text{H}} + \beta_{\text{S}} T] \text{F} \right). \text{ From this latter relation, } d\beta/dT \text{ follows obviously as }
\]

\[
d\beta/dT = 2.3 \text{RT}/[(\beta_{\text{H}} + T\beta_{\text{S}})^2 \text{F}] \tag{2}
\]

\( \beta \) can never be negative since it represents the direct effect of potential on the energy of activation \( (\Delta H_\text{F}^+ = \Delta H_\text{F}^\text{int} + \beta_{\text{H}} \text{VF}) \) which always decreases with increasing numerical value of the potential (in the negative direction for a cathodic process). Since the term \( (\beta_{\text{H}} + T\beta_{\text{S}})^2 \) must always be positive, it is clear that (2), based on the relation \( \beta = \beta_{\text{H}} + T\beta_{\text{S}} \), can never account for the direction of change of \( b \) values with temperature for proton transfer at Au from the \( \text{H}_3\text{O}^+ \) melt or the \( \text{H}_5\text{O}_2 \) hydrate.

\[
\text{Fig. 13. Dependence of } \log i_0 \text{ and } b \text{ values for the } \text{H}_2 \text{ evolution reaction at Au on the speciation of the proton hydrates.}
\]

* The only formal possibility for \( d\beta/dT \) to be negative is if the \( T \) factor within the \( \beta_{\text{H}} + T\beta_{\text{S}} \) term in (2) has a power > 1. This is physically unlikely, as is also the possibility that \( \beta_{\text{S}} \) is itself proportional to \( T \) to a power > 0.
dence of the log of the frequency factor, i.e. of a component of the apparent $\Delta S^\circ$. However, this will appear also nominally as a $\beta_s$ term, or a component of it, so again, on the basis of (2), could not account for negative values of $db/dT$.

For the above reasons, we must suppose that the negative $db/dT$ arises from a temperature-dependent structural aspect of the double-layer in the $H_3O^+$ melt and for the $H_2SO_4$ solution, connected e.g. with the potential profile across the region of distributed, partially hydrated $H_2O^+$ cations and $CF_3SO_3^-$ anions at the electrode interface, an effect which will presumably be dependent on electrode surface charge-density and on temperature.

**Acknowledgement**

Support of this work by the Natural Sciences and Engineering Research Council of Canada through the establishment of the Alcan-N.S.E.R.C.C. Research Chair of Electrochemistry at University of Ottawa is gratefully acknowledged.