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Electrochemical Impedance Spectroscopy Study of the Response Mechanism of the Jalpaite Cu^{II} Ion-Selective Electrode in Seawater

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This paper presents the results of a novel study into the response mechanism of the jalpaite copper(II) ion-selective electrode (ISE) using electrochemical impedance spectroscopy (EIS) under conditions of minimal overpotential stimulation (i.e., ±10 mV). The EIS spectra of the jalpaite ISE in seawater and other ionic media revealed a high-frequency surface film impedance that is attributable to the modified hydrated surface layers of the ISE, and a low-frequency charge-transfer impedance that can be ascribed to the reductive ion-exchange of Cu^{II} at the membrane/electrolyte interface. EIS data for a rotating disk electrode have shown that the charge-transfer process is under diffusion control. EIS and potentiometric response data in UV-oxidized seawater spiked with humic acid imply that organic complexation of Cu^I at the electrode diffusion layer is responsible for a weak interference effect. The classical chloride interference effect of the jalpaite Cu^{II} ISE occurring at high concentrations of Cu^{II} (i.e., > 10^{-6} M) yields an EIS response similar to the one observed with organic ligands. An EIS experiment for a jalpaite Cu^{II} ISE aged in seawater for 72 h demonstrated that the charge-transfer impedance is constant until electrode release of Cu^{II} exceeds the complexing capacity of seawater, and this mechanistic information is consistent with the hypothesis that electrode dissolution can be used to autotitrate the natural ligands in seawater.

Existing knowledge on the response mechanism of the jalpaite copper(II) ion-selective electrode (ISE) is limited to indirect evidence obtained in various potentiometric response studies. Pertinent aspects of these investigations have been summarized in two excellent reviews by Gulens.[1,2] Essentially, the accepted theory of electrode response entails the reductive ion-exchange

of Cu^{II} at CuS sites within the membrane diffusion layer, viz.,

$$Cu^{2+}_{(aq)} + CuS_{(s)} \rightarrow 2Cu^+_{(aq)} + S_{(s)} \qquad (I)$$

It is proposed that the Cu^I ion-conducting membrane responds directly to Cu^I released at the electrode diffusion layer, and the Cu^{II} response is characterized by an equilibrium constant for the above-mentioned side reaction. Actually, Stunzi[3] has shown that the jalpaite Cu^{II} ISE responds in a Nernstian manner to Cu^I (i.e., 61.6 mV/decade) in aqueous acetonitrile solutions, and his potentiometric response data enabled a determination of the selectivity coefficient for Cu^{II}, viz., log $K^{pot}_{i,j}$ = −6.48. Several other authors[4,5] have obtained similar values for the Cu^{II} selectivity coefficient (viz., log $K^{pot}_{i,j}$ = −5.9 to −6.4).

Several key papers[6−8] have rationalized electrode interference effects using the above-mentioned reductive ion-exchange theory. Westall et al.,[6] along with Lewenstam et al.,[7] explained the chloride interference of the Cu^{II} ISE by postulating the following reaction mechanism:

$$Cu^{2+}_{(aq)} + CuS_{(s)} \rightarrow 2Cu^+_{(aq)} + S_{(s)} \qquad (II)$$

$$Cu^+_{(aq)} + nCl^-_{(aq)} \rightarrow CuCl_n^{1-n}_{(aq)} \qquad (III)$$

The complexation of Cu^I by chloride diminishes the level of Cu^I at the electrode diffusion layer, shifting the electrode potential toward more negative values.

Although recent work by Belli and Zirino[9] along with De Marco[10] has demonstrated that the potentiometric response of the jalpaite Cu^{II} ISE is collinear in a variety of saline-buffered media (e.g., synthetic seawater, Cu^{II}-glycine, Cu^{II}-ethylenediamine, etc.), there are suggestions in the literature[11,12] that the ligands of Cu^{II}

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(1) Gulens, J. *Ion-Sel. Electrode Rev.* **1981,** *2,* 117−57.
(2) Gulens, J. *Ion-Sel. Electrode Rev.* **1987,** *9,* 127−71.
(3) Stunzi, H. *Talanta* **1982,** *29,* 75−6.
(4) Hulanicki, A.; Trojanowicz, M.; Cichy, M. *Talanta* **1976,** *23,* 47−50.
(5) Neshkova, M.; Sheytanov, H. *Talanta* **1985,** *32,* 654−6.
(6) Westall, J. C.; Morel, F. M. M.; Hume, D. N. *Anal. Chem.* **1979,** *51,* 1792−8.
(7) Lewenstam, A.; Sokalski, T.; Hulanicki, A. *Talanta* **1985,** *32,* 531−7.
(8) Lanza, P. *Anal. Chim. Acta* **1979,** *105,* 53−65.
(9) Belli, S. L.; Zirino, A. *Anal. Chem.* **1993,** *65,* 2583−9.
(10) De Marco, R. *Anal. Chem.* **1994,** *66,* 3202−7.
(11) Hoyer, B. *Talanta* **1991,** *38,* 115−8.

ion buffer systems exert an influence similar to the chloride interference effect (i.e., chelation of Cu^I leads to a negative offset in ISE potential). De Marco[10] noted a shift in standard electrode potential for a copper selenide Cu^{II} ISE, and a key paper by Hoyer[11] also revealed a sensitivity toward complexing ligands for the copper selenide Cu^{II} ISE. It is highly probable that the ligand interference effect is restricted to the copper selenide Cu^{II} ISE.[13] It is also important to note that the absence of a chloride interference effect for the jalpaite Cu^{II} ISE in saline metal ion buffers[9,10] is probably due to severe kinetic limitations of the interference reaction at extremely low concentrations of Cu^{2+} (i.e., $<10^{-10}$ M).[10]

Despite the consensus on the role of a charge-transfer process in controlling the potential of the Cu^{II} ISE, there have been limited studies into the electrode kinetics of this analytically important system. Lewenstam and co-workers[14,15] have used cyclic voltammetry to study the electrodissolution of CuS in chloride-based media. This experimental approach may significantly perturb the electrode system since the application of a substantial overpotential is required for the stimulation of a potentiodynamic signal, and this scenario does not necessarily produce mechanistic information pertaining to potentiometry at near zero current.

The main aim of this study was to carry out an electrode kinetic study of the response mechanism of the jalpaite membrane Cu^{II} ISE using an electrochemical technique that does not perturb the electrode system [i.e., electrochemical impedance spectroscopy (EIS) at low overpotentials of ± 10 mV]. First, the EIS spectra for some well-characterized phenomena (i.e., chloride interference and Cu^{II} sensitivity) have been used to determine the suitability of this approach to a mechanistic study of the jalpaite Cu^{II} ISE. Second, the influence of organic ligands on the response of the jalpaite Cu^{II} ISE in seawater has been studied to ascertain the implications of ligand effects on the analysis of Cu^{II} in seawater. Last, the kinetics of the diffusion-controlled charge-transfer process of the jalpaite Cu^{II} ISE in seawater has been investigated using a rotating disk electrode (RDE).

EXPERIMENTAL SECTION

Reagents. Analytical grade inorganic reagents were used in all cases, and solutions were made up in ultrahigh-purity Milli-Q water. A technical grade sodium salt of humic acid (supplied by Aldrich Chemical Co.) was used in this study.

Electrodes. Three types of copper ion-selective electrode were used in this study: (i) a static jalpaite sensor was fabricated using a jalpaite powder that was prepared by coprecipitation of CuS and Ag_2S in the presence of 20% excess Na_2S;[16] (ii) a RDE jalpaite sensor was fabricated using a powder that was prepared by coprecipitation of CuS and Ag_2S in the presence of 80% excess Na_2S;[16] (iii) a commercial ORION Cu^{II} ISE (model 94-29) was purchased that utilizes a pressed disk of jalpaite as its membrane.[17]

(12) Hulanicki, A.; Krawczynski, T.; Lewenstam, A. *Anal. Chim. Acta* **1984**, *158*, 343−55.

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(14) Ghali, E.; Dandapani, B.; Lewenstam, A. *J. Appl. Electrochem.* **1982**, *12*, 369−76.

(15) Lewenstam, A.; Hulanicki, A.; Ghali, E. In *Contemporary Electroanalytical Chemistry*; Ivaska, I., et al., Eds.; Plenum Press: New York, 1990; pp 213−22.

(16) Heijne, G. J. M.; Van Der Linden, W. E. *Anal. Chim. Acta* **1977**, *93*, 99−110.

(17) Siemroth, J.; Hennig, I. *Anal. Chem. Symp. Ser.* **1981**, *8*, 339−48.

For electrode types i and ii, a jalpaite disk was pressed in a Specac punch and die at 10 tons or 7.9×10^5 kPa. A silver epoxy contact was attached to one side of the disk, and the membrane was sealed into an electrode body using a clear epoxy resin. Although the variation in membrane composition affected the bulk membrane resistance and EIS response characteristics of each electrode, it was found that the EIS trends (relative to a control) for various effects (e.g., chloride, humic acid, pH, etc.) were comparatively similar for all electrodes.

EIS Studies. EIS studies on Cu^{II} ISEs (polished on Struers 1-μm diamond spray and Struers red lubricant) were undertaken using an EG&G Princeton Applied Research model 5120 potentiostat equipped with a lock-in amplifier. The EIS spectra were recorded using an overpotential window of ± 10 mV and a frequency range from 100 kHz to 1 mHz. A conventional three-electrode cell was used in the EIS studies [viz., a Cu^{II} ISE as the working electrode, a platinum counter electrode, and a saturated calomel electrode (SCE) as the reference]. For the RDE studies, a membrane was attached to a threaded aluminum stub using silver epoxy that was subsequently encapsulated in a clear epoxy resin. The cured RDE was inserted into a single-element PINE electrode rotator (model AFCPRB). All EIS spectra were fitted to equivalent circuits using the equivalent circuit program of Boukamp.[18]

RESULTS AND DISCUSSION

EIS Studies on a Static Cu^{II} ISE. The EIS response of two static Cu^{II} ISEs was studied in unbuffered Cu^{II} standards and UV-oxidized seawater spiked with commercial humic acid. This work was undertaken to verify the applicability of EIS to a study of the electrode kinetics of the Cu^{II} ISE, and to examine the influence of natural seawater ligands on the response of the Cu^{II} ISE.

Cu^{II} Response. Figure 1a presents EIS Nyquist plots for a static Cu^{II} ISE in $Cu(NO_3)_2$ standards in 0.1 M KNO_3. The spectrum in 10^{-5} M $Cu(NO_3)_2$ reveals a high-frequency surface film impedance that is probably associated with Cu^{II} ions residing within the modified surface layers of the jalpaite membrane (i.e., hydrated membrane/electrolyte interface). Another semicircle that can be ascribed to a charge-transfer impedance (i.e., R_t) is discernible at low frequencies. It is important to note that the rate of the charge-transfer process is inversely proportional to R_t.

The EIS spectra were fitted to the equivalent circuit shown in Figure 2a, yielding the circuit elements presented in Table 1. The constant-phase elements (CPE) Q_1 and Q_2 are described by parameters n_1 and n_2, with impedances, Warburg terms, capacitances, and inductances being defined by $n = 0$, 0.5, 1, and -1, respectively.[18] It must be noted that the Boukamp results convey the incorrect impression that the solution impedance is dependent on the concentration of Cu^{II}. In all cases, the solution impedance (around 100 Ω) is significantly lower than the film and charge-transfer impedances (about 0.1 and 1 MΩ, respectively), and the apparent variation in solution impedance is due to limitations with the Boukamp algorithm in deconvoluting severely overlapped large film and charge-transfer impedances from a low solution impedance. By contrast, the diminution in surface film impedance at higher concentrations of Cu^{II} is consistent with the presence

(18) Boukamp, B. A. In *Equivalent Circuit, Users Manual*, 2nd ed.; University of Twente: The Netherlands, 1993.

Table 1. Boukamp Equivalent Circuit Parameters for a Static Cu^{II} ISE (Fitted to the Circuit Presented in Figure 2a) in Cu(NO$_3$)$_2$ Standards also Containing 0.1 M KNO$_3$, and UV-Oxidized Seawater Spiked with 1, 10, 50, and 100 ppm of Humic Acid

solution	R_{soln} (Ω)	Q_1 ($\times 10^{-9}$ Ω^{-1} s^n)	n_1	R_{film} (MΩ)	Q_2 ($\times 10^{-7}$ Ω^{-1} s^n)	n_2	R_t (MΩ)
10^{-5} M Cu	129	2.25	0.97	0.124	1.32	0.62	1.47
10^{-3} M Cu	48	1.60	1.00	0.089	0.934	0.56	1.43
10^{-1} M Cu	48	1.79	0.99	0.100	0.916	0.57	1.35
UV	143	1.64	1.00	0.151	1.15	0.64	1.36
UV + 1 ppm	155	1.63	1.00	0.146	1.17	0.64	1.28
UV + 10 ppm	152	1.63	1.00	0.141	1.22	0.63	1.17
UV + 50 ppm	149	1.66	1.00	0.132	1.26	0.63	1.02
UV + 100 ppm	74	1.74	0.99	0.129	1.27	0.63	0.96

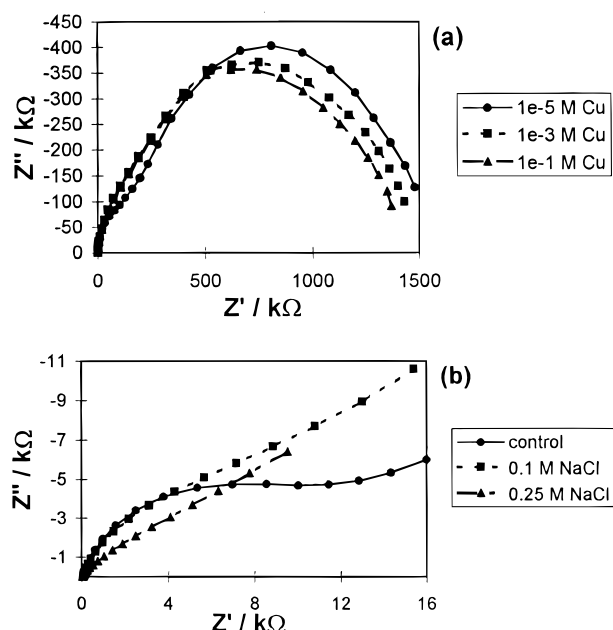**Figure 1.** EIS spectra for (a) a static Cu^{II} ISE in Cu(NO$_3$)$_2$ standards in 0.1 M KNO$_3$ and (b) a commercial ORION Cu^{II} ISE in 10^{-5} M Cu-(NO$_3$)$_2$ plus 0.1 M KNO$_3$ spiked with different levels of NaCl.

Figure 2. Equivalent circuits for Cu^{II} ISE systems: (a) static Cu^{II} ISE; (b) static commercial ORION Cu^{II} ISE; (c) RDE Cu^{II} ISE.

Table 2. Boukamp Equivalent Circuit Parameters for a Static Commercial ORION Jalpaite Cu^{II} ISE (Fitted to the Circuit Presented in Figure 2b) in 10^{-5} M Cu(NO$_3$)$_2$ plus 0.1 M KNO$_3$ Spiked with 0.1 and 0.25 M NaCl

solution	R_{soln} (Ω)	Q_2 ($\times 10^{-4}$ Ω^{-1} s^n)	n_2	R_t (kΩ)	W (mΩ^{-1})
no NaCl	126	0.632	0.85	11.0	0.54
0.1 M NaCl	72.4	0.985	0.84	8.1	0.27
0.25 M NaCl	59.8	1.58	0.79	3.94	0.33

of a Cu^{II}-exchanged hydrated surface film that is more conductive as it becomes loaded with Cu^{II} ions at elevated levels of Cu^{II}. Note that this Cu^{II} ISE EIS response study was carried out in duplicate, and all equivalent circuit parameters agreed to within $\pm 2-6\%$ (relative) of the average value. It can be shown that the Cu^{II} concentration dependency of R_t (i.e., reduction in R_t or increase in the rate of charge transfer at elevated levels of Cu^{II}) is consistent with the accepted reductive ion-exchange theory for the response of the Cu^{II} ISE, viz.,

$$CuS_{(s)} \rightarrow Cu^+{}_{(aq)} + S_{(s)} + e \qquad (IV)$$

$$Cu^{2+}{}_{(aq)} + e \rightarrow Cu^+{}_{(aq)} \qquad (V)$$
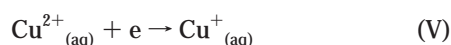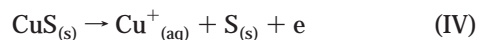
As expected, the charge-transfer impedance of the Cu^{II} ISE diminishes at elevated levels of Cu^{II} as these conditions favor the kinetics of the forward process of the charge-transfer reaction.

Chloride Interference. The EIS Nyquist plots for a static ORION Cu^{II} ISE in 10^{-5} M Cu(NO$_3$)$_2$ and 0.1 M KNO$_3$ spiked with various levels of NaCl are presented in Figure 1b, and the Boukamp equivalent circuit parameters (fitted to the equivalent circuit given
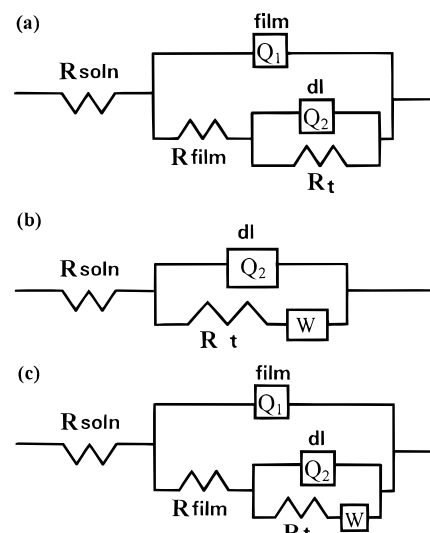
in Figure 2b) are shown in Table 2. It can be seen that the charge-transfer impedance decreases (or the charge-transfer rate increases) as the Cu^{II} standard is spiked with NaCl, and this outcome is consistent with the accepted mechanism for the chloride interference effect whereby Cu^{I} formed by reactions IV and V is complexed by chloride (see reaction III). Under these conditions, the rate of the reverse charge-transfer process is diminished, leading to an increase in the net rate of the charge-transfer reaction.

It is important to note that, under saline conditions, the static ORION Cu^{II} ISE yields a substantial Warburg impedance at low frequency (i.e., 45° line at the low-frequency end of the EIS Nyquist plot presented in Figure 1b), and this severe spectral overlap precludes a direct resolution of the interfacial circuit components of the Cu^{II} ISE in the raw spectrum (i.e., solution, surface film, charge-transfer, and Warburg impedances). The contribution of an intense diffusion-controlled process is expected,
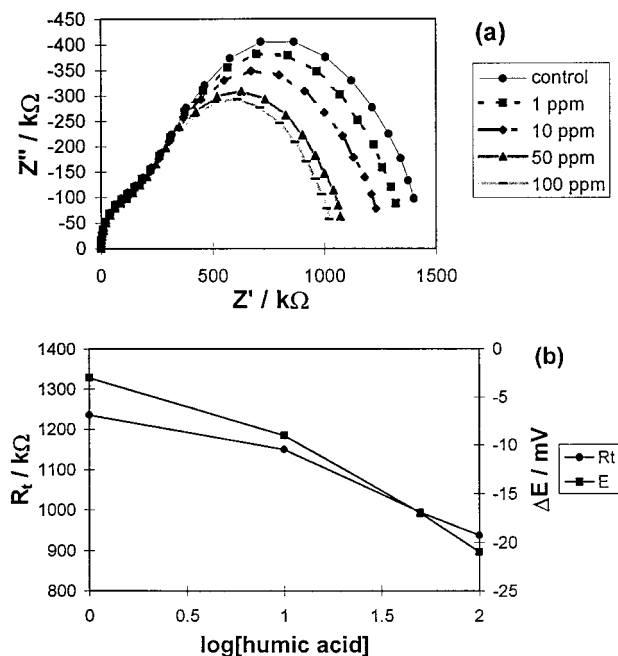
Figure 3. EIS spectra for a static Cu[II] ISE in UV-oxidized seawater spiked with different levels of commercial humic acid (viz., a) and trends in electrode potential and charge-transfer impedance (b).

as Jasinski et al.[19] have shown that the electrode response is strongly dependent on the stirring rate in saline solutions. Despite this problem, the Boukamp equivalent circuit software is able to partially deconvolute the solution, charge-transfer, and Warburg impedances but provides a nil result for the surface film. The lack of a surface film impedance for the static ORION Cu[II] ISE is probably attributable to the inability of the Boukamp software to discriminate between equivalent circuit components having similar EIS frequency responses (i.e., solution and film impedances) when a substantial Warburg impedance obscures the EIS response at high frequency.

The difference in EIS response for the two static electrodes (see Tables 1 and 2) is attributable to variations in the composition and bulk electrical conductivities of their membranes [viz., the noncommercial system comprises jalpaite along with small amounts of covellite (i.e., CuS) and acanthite (i.e., Ag_2S),[16] while the ORION Cu[II] ISE comprises a membrane of jalpaite[17]]. It was found that the bulk electrical resistances of the two systems differed by approximately 2 orders of magnitude, with the fabricated electrode having the higher resistance at about 1 MΩ. As expected, the rate of charge transfer at the more resistive noncommercial electrode is significantly lower, as reflected by the considerable increase in the charge-transfer impedance (see Tables 1 and 2).

Humic Acid Interference. Figure 3a presents the EIS Nyquist plots for the static Cu[II] ISE in organic-free, UV-oxidized seawater that has been spiked with varying amounts of commercial humic acid, and equivalent circuit parameters (fitted to the equivalent circuit given in Figure 2a) are shown in Table 1. There are two notable features in the EIS spectra. First, the surface film impedance is more discernible in seawater compared to $Cu(NO_3)_2$ standards (compare with Figure 1a), and this is consistent with a

less conductive hydrated surface film that is depleted with respect to Cu[II] ions at trace levels of Cu[II] in seawater. Second, the charge-transfer impedance is reduced (or the charge-transfer rate is enhanced) at higher concentrations of humic acid, and the similarities in charge-transfer impedance and electrode potential trends (refer to Figure 3b) demonstrate that the rate of the charge-transfer reaction is the potential determining process for the organic ligand interference effect. Significantly, the potentiometric response data presented in Figure 3b suggest that the seawater organic ligand interference effect is weak; i.e., 1 ppm of humic acid (i.e., the typical level in seawater) induces a −3 mV or + 0.1 pCu unit change in the potential of the Cu[II] ISE. As was the case for the Cu[II] EIS response of the Cu[II] ISE, the EIS data for duplication of the humic acid interference study yielded electrical properties that agreed within ±2−6% (relative) of average values.

The following mechanism has been proposed to explain the interference effect of organic ligands in seawater (viz., chelation of Cu[I] formed via reactions IV and V):
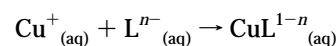
$$Cu^+_{(aq)} + L^{n-}_{(aq)} \rightarrow CuL^{1-n}_{(aq)}$$

Under these conditions, the rate of the reverse charge-transfer process is diminished, leading to an increase in the net rate of the charge-transfer reaction. It is important to note that complexation of Cu[II] by added humic acid is unlikely, as the speciation of trace metals in seawater is under kinetic control.[20] This scenario is made more credible if one considers that the complexation of Cu[II] will favor the reverse charge-transfer reaction, leading to a decrease, not the observed increase, in the net rate of the charge-transfer process.

EIS Studies on a RDE. The diffusion-controlled charge-transfer process of the Cu[II] ISE was studied using a polished RDE that was conditioned in UV-oxidized seawater for 1 h to give a steady-state signal. The long-term effects of organic ligands were also examined using a polished RDE that had been conditioned in raw seawater for 24 h to ascertain the effects of electrode ablation at high rotation speed. Zirino et al.[21] have proposed that electrode release of Cu[II] arising through membrane corrosion may enable autotitrations of seawater ligands, and this approach may be applicable to determinations of seawater Cu[II]-complexing capacities. The theoretical validity of the autotitration approach has been investigated using EIS in conjunction with an RDE that had been conditioned in three separate samples of UV-oxidized seawater for 9 h during the accumulation of repeatable and reliable control EIS spectra. A RDE was chosen for the autotitration study, as the long-term aging of a jalpaite Cu[II] ISE in seawater can lead to severe AgCl fouling of the sensor,[22] and the effects of electrode ablation at high rotation speed can minimize the detrimental effects of AgCl poisoning. Indeed, the RDE aged in seawater did not display the common visual signs of AgCl fouling (i.e., membrane tarnishing).

Effect of Rotation Speed. Figure 4 shows the Nyquist plots for a RDE Cu[II] ISE in raw seawater containing natural organic ligands. All RDE Cu[II] ISE EIS spectra were fitted to the equivalent circuit

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(20) Mackey, D. J.; Zirino, A. *Anal. Chim. Acta* **1994**, *284*, 635−47.

(21) Zirino, A.; Belli, S. L.; Van Der Weele, D.; De Marco, R.; Mackey, D. J. *Mar. Chem.* **1998**, *61*, 173−84.

(22) De Marco, R. *Mar. Chem.* **1996**, *55*, 389−98.

Table 3. Boukamp Equivalent Circuit Parameters for a RDE Jalpaite Cu^{II} ISE (Fitted to the Circuit Presented in Figure 2c) in Natural Seawater at Different Rotation Speeds and after Aging in UV-Oxidized Seawater Spiked with 1 ppm of Humic Acid (1600 rpm)

| solution	R_{soln} (Ω)	Q_1 ($\times 10^{-7}$ Ω^{-1} s^n)	n_1	R_{film} (kΩ)	Q_2 ($\times 10^{-4}$ Ω^{1-} s^n)	n_2	R_t (kΩ)	W (Ω^{-1})
sea, 1000 rpm	neg	1.14	0.68	3.92	1.54	0.89	38.6	1.3×10^{13}
sea, 4000 rpm	neg	1.24	0.67	3.68	1.28	0.88	10.4	2.2×10^{13}
sea, 6000 rpm	neg	1.09	0.68	3.48	1.31	0.88	5.5	2.8×10^{13}
age (3 h)	neg	0.905	0.75	11.2	0.444	0.86	186	2.6×10^{-3}
age (6 h)	neg	0.897	0.74	10.7	0.361	0.87	184	1.3×10^{-3}
age (9 h)	neg	0.838	0.75	10.2	0.325	0.88	156	1.5×10^{-3}
age (12 h)	neg	0.830	0.75	10.1	0.305	0.88	104	3.8×10^{-3}
age (15 h)	neg	0.884	0.74	9.7	0.295	0.88	75.3	7×10^{-3}

[a] neg = negligible.
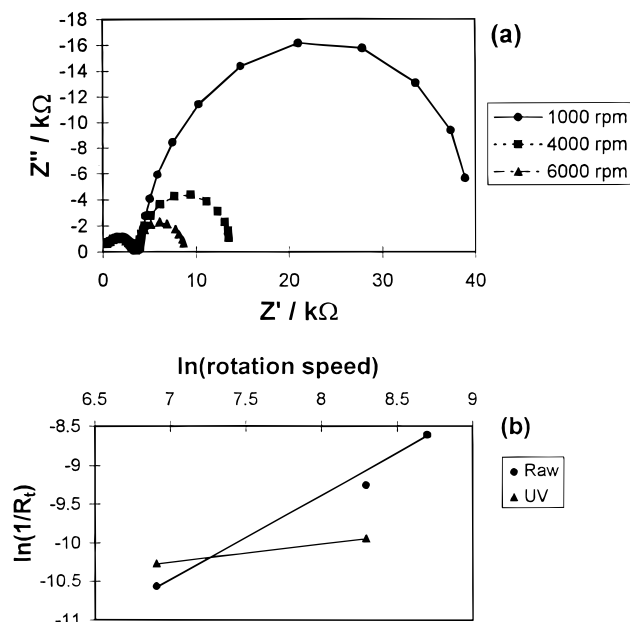
Figure 4. EIS spectra for a RDE Cu^{II} ISE (aged in natural seawater for 24 h) in natural seawater at various rotation speeds (viz., a) and plots of ln(1/R_t) versus ln(rotation speed) (b).

presented in Figure 2c using the Boukamp program, and the results are shown in Table 3. As expected for a diffusion-controlled process, the charge-transfer reaction of the Cu^{II} ISE is facilitated at high rotation speed; however, a slope of 1.1 for the plot of ln(1/R_t) versus ln(rotation speed) in Figure 4b does not comply with the value of 0.5 predicted by the Levich equation.[23] By contrast, the considerably lower slope in organic-free, UV-oxidized seawater (i.e., ∼0.3; refer to Figure 4b) is closer to the expected value for the Levich equation.

The nonconformity of the RDE to the Levich equation in raw seawater is symptomatic of a ligand adsorption phenomenon that can be ameliorated at high rotation speed. It is likely that the desorption of organic ligands occurring at high rotation speed dilutes the concentrations of ligands within the electrode diffusion layer, and the corresponding reduction in Cu^{II} complexing capacity at the electrode surface accentuates the sensitivity of R_t to rotation speed (i.e., slope > 0.5). Significantly, Zirino et al.[21] also studied the variation in potential at a RDE in San Diego Bay seawater at

(23) Levich, V. In *Physicochemical Hydrodynamics*; Prentice Hall: Englewood Cliffs, NJ, 1962.

pH 8, noting that the potential was practically static at low rotation speeds (i.e., from 60 to 2000 rpm) in ascending order, but the trend in a consecutive descending run from 6000 to 60 rpm obeyed the Levich equation. The findings by EIS and Zirino et al.[21] strongly suggest that the effects of ligand adsorption on the jalpaite membrane can be overcome irreversibly through ablation of the electrode surface at high rotation speed at a RDE.

It is important to note that the EIS equivalent circuits for the static and RDE Cu^{II} ISEs are quite different, despite the similarities in membrane preparation (i.e., sulfide-based precipitation from a Cu(NO$_3$)$_2$/AgNO$_3$ mixture). The static system was prepared by employing a 20% excess of sulfide during precipitation, and these conditions favored the formation of jalpaite along with small amounts of covellite (i.e., CuS) and acanthite (i.e., Ag$_2$S).[16] By contrast, the RDE formed by precipitation in 80% excess sulfide is composed almost entirely of jalpaite.[16] As was the case for the static ORION and fabricated electrodes, the electrical resistances of the fabricated static electrode and RDE systems differed by approximately 2 orders of magnitude, with the static electrode having the higher electrical resistance at about 1 MΩ, leading to a considerable increase in the charge-transfer impedance for the latter system (see Tables 1 and 3). Additionally, the EIS response of the RDE system under static conditions (not shown) was identical to that for the static ORION Cu^{II} ISE in saline solutions (i.e., a substantial low-frequency Warburg impedance obscured the EIS spectra; see Figure 1b), and this was expected, as both membranes consisted entirely of jalpaite. Although the Warburg impedance is diminished to a very low level at an RDE (viz., 10^{13} Ω^{-1}; see Table 3), the inclusion of a small Warburg impedance term in the equivalent circuit was needed to obtain a good correlation between Boukamp fitted and experimental data. Presumably, this is due to the Warburg impedance providing a small but real contribution to the EIS response of the RDE at low frequency.

A second important outcome of the effect of rotation speed on a RDE aged in raw seawater is the significant diminution in charge-transfer and Warburg impedances (at 1000 rpm) compared to those of an RDE that has been aged in organic-free, UV-oxidized seawater (compare Figures 4a and 6a and data presented in Table 3). Significantly, the charge-transfer impedance at 4000 rpm for an RDE aged in raw seawater is similar to that for a polished RDE in UV-oxidized seawater (compare Figures 4a and 5a). In accordance with De Marco's X-ray photoelectron spectroscopy (XPS)
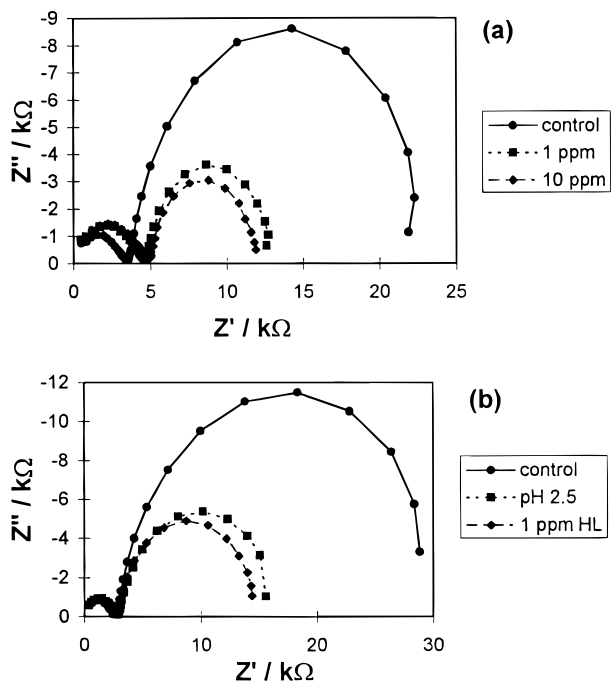
Figure 5. EIS spectra for a polished RDE Cu^{II} ISE rotated at 4000 rpm in (a) UV-oxidized spiked with commercial humic acid at natural pH and (b) UV-oxidized seawater acidified to pH 2.5 and spiked with 1 ppm humic acid.

Figure 6. EIS spectra for a RDE Cu^{II} ISE (aged in UV-oxidized seawater for 9 h) rotated at 1600 rpm at various stages of aging in UV-oxidized seawater spiked with 1 ppm humic acid (viz., a) and trends in electrode potential and charge-transfer impedance (b).

work, which showed that adsorbed organic surfactants promote the peptization of AgCl, alleviating electrode fouling in seawater, the EIS findings strongly suggest that seawater organic ligands ameliorate the effects of electrode aging in seawater. This idea will be developed further in a discussion of EIS results for a RDE aged in UV-oxidized seawater (see Electrode Aging in Seawater).

Humic Acid Interference. It is evident that rotation of the Cu^{II} ISE at 4000 rpm (refer to the EIS Nyquist plots for the RDE in UV-oxidized seawater presented in Figure 5a) either facilitates the desorption of organic ligands, diminishing the ligand concentration and corresponding Cu^{II} complexing capacity in the electrode diffusion layer, or accentuates the humic acid interference effect as the charge-transfer impedance is halved by the addition of 1 ppm humic acid for a RDE, compared to a few percent change in R_t at the static ISE (compare with Figure 3a). Significantly, the substantial decrease in the charge-transfer impedance for the RDE Cu^{II} ISE in UV-oxidized seawater at pH 2.5 (see Figure 5b) is consistent with an increase in the level of free Cu^{II} as protonation of seawater ligands dissociates Cu^{II} complexes. Even under acidic conditions, the addition of 1 ppm of commercial humic acid leads to a mild interference effect (i.e., a slight diminution in the charge-transfer impedance), but the interference is considerably weaker at pH 2.5 (as evidenced by a smaller change in R_t in acidic seawater). Undoubtedly, the electrode error noted by De Marco et al.[24] for determinations of total Cu^{II} in acidified seawater in the presence of natural organic ligands is attributable to the above-mentioned interference phenomenon. Significantly, the EIS response of the RDE to additions of humic acid is identical to that for the static Cu^{II} ISE (compare Figures 3a and 5a), demonstrating that a variation in membrane composition affects only the
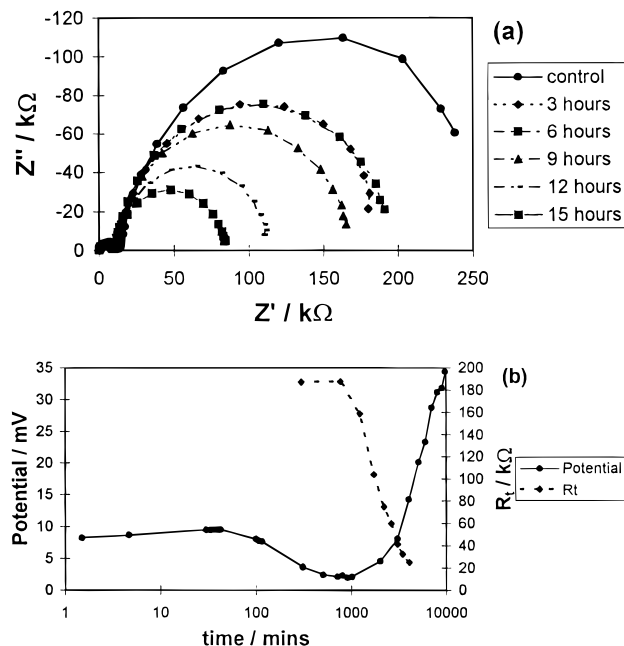
membrane resistance and absolute values of equivalent circuit parameters, not the trend relative to a control experiment.

Electrode Aging in Seawater. Figure 6 presents EIS Nyquist plots and the charge-transfer impedance–time trend for a seawater-aged RDE Cu^{II} ISE (9 h) that has been aged in UV-oxidized seawater spiked with 1 ppm of commercial humic acid. Also included in Figure 6b is a segment of a potential–time trend presented by Zirino et al.[21] for the autotitration of San Diego Bay seawater using an ORION Cu^{II} ISE. The corresponding equivalent circuit parameters (fitted to the equivalent circuit given in Figure 2c) are also shown in Table 3. It is evident that the charge-transfer impedance is relatively constant over the first 6 h and diminishes significantly on continuous aging in seawater. It is important to note that the decrease in R_t is consistent with ISE response to electrode release of Cu^{II} ions. The variation in potential (extracted from Zirino et al.[21] for a San Diego Bay sample) is mirrored by the change in charge-transfer impedance in humic acid-spiked, UV-oxidized seawater. Although the samples are different, it is expected that the resultant trends will be similar, albeit that an offset may exist between the two samples.

A second important feature of the EIS Nyquist plot for the control in this experiment (i.e., jalpaite Cu^{II} ISE aged in UV-oxidized seawater for 9 h presented in Figure 6a) compared to the one for a polished jalpaite ISE in UV-oxidized seawater (see Figure 5) is the significant enhancement in charge-transfer and Warburg impedances (see Table 3). This is expected because previous XPS work[22] has demonstrated that small amounts of harmless and insulating AgCl are formed on jalpaite that has been exposed to seawater for long periods, and this is expected to act like a passivation layer, diminishing the rate of the charge-transfer process (or increasing the charge-transfer impedance). This suggestion is also supported by the fact that AgCl is known to invoke a diffusion-controlled process that manifests itself as a

(24) De Marco, R.; Mackey, D. J.; Zirino, A. *Electroanalysis* **1997**, *9*, 330–4.

sensitivity of the jalpaite Cu^{II} ISE to stirring rate,[19] and this phenomenon is expected to yield the observed increase in Warburg impedance with the seawater-aged RDE.

The EIS data for the aged RDE Cu^{II} ISE in seawater are internally consistent with the hypothesis of Zirino et al.[21] that it is possible to employ the break-point in the ISE autotitration of natural ligands in seawater (attributable to electrode release of Cu^{II}) as a novel means of determining Cu^{II}-complexing capacities. Clearly, the charge-transfer process and corresponding electrode potential in the initial stages of aging are static because, under these conditions, seawater possesses sufficient Cu^{II} buffering ability; however, the ISE senses the electrode release of Cu^{II} (signaled by a decrease in R_t) once the Cu^{II} complexing capacity of the seawater has been exceeded.

Significantly, Zirino et al.[21] have also measured the rate of dissolution of the jalpaite Cu^{II} ISE over the duration of the aging experiment using atomic absorption spectrometry, noting a constant Cu release rate of 1.7×10^{-2} nM min^{-1}. These data show that the break-point (1000 min) corresponds to the injection of 17 nM Cu, and, as expected, near-Nernstian response (i.e., 32 mV/decade) occurs beyond the break-point (i.e., between 1000 and 10 000 min). As was the case for the Cu^{II} ISE study in unbuffered Cu standards (see Figure 1a), the EIS response beyond the autotitration break-point is consistent with an enhancement in the kinetics of the charge-transfer process at elevated levels of Cu.

CONCLUSIONS

The results of this study demonstrate unambiguously that the response of the jalpaite Cu^{II} ISE is underpinned by the Cu^{II}/Cu^{I} charge-transfer process occurring at the membrane/electrolyte interface. A weak ligand interference effect arises through the complexation of Cu^{I} at the electrode diffusion layer; consequently, the organic ligands of seawater do not pose a serious problem for seawater analyses.

The EIS data provide conclusive evidence that the break-point in an autotitration of seawater through electrode dissolution of the Cu^{II} ISE is related to the Cu^{II}-complexing capacity of the sample. In addition, the RDE Cu^{II} ISE data suggest that ablation of the electrode at high electrode rotation speed may minimize the effects of adsorbed organic ligands on the response of the Cu^{II} ISE in seawater.