Ionic liquid enhanced electrochemical characterization of organic coatings

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\textbf{Abstract}

Our laboratory recently began work on the use of room temperature ionic liquids ((RTIL’s) to enhance our capabilities for the electrochemical characterization of organic coatings \cite{Simoes2005}. The RTIL’s are electrically conductive liquids consisting of large molecules that can be used to investigate the electrochemical properties of coatings in a non-aqueous medium. The enhancement of coating characterization comes from the fact that RTIL’s have sufficient conductivity to be an immersion medium for electrochemical measurements, but they do not directly penetrate and effect organic coatings as do aqueous electrolyte solutions. This allows the separate examination of the effects of water on coatings in immersion or cyclic exposure. Indeed, our initial studies showed that a hydrophilic RTIL could be used to electrochemically characterize the drying of a coating after immersion, a process which heretofore had not been followed electrochemically. Thus, electrochemical measurements of coatings based on aqueous electrolyte immersion can be enhanced by the use of RTIL’s and the effects of water on the coatings under study isolated and analyzed separately, especially the diffusion of water out of coatings during drying processes. Recent papers from our group have introduced the methodology whereby RTIL’s in conjunction with capacitance monitoring via electrochemical impedance spectroscopy (EIS) can be used to determine the diffusion coefficient of water out of a non-pigmented, additive free coating \cite{Simoes2005, Allahar2007, Bierwagen2006, Hinderliter2008}. The technique has been extended to several types of coatings as well as the study of the cyclic wetting and drying of coatings \cite{Allahar2007, Bierwagen2006}. This latter set of processes is one of the key set of events in exterior exposure that causes the failure of exterior protective coatings. Recently, RTIL’s have been used to simulate the alternate wetting and drying of a Zn-rich epoxy coating system. EIS experiments were conducted on the Zn-rich epoxy under constant immersion in 0.05 M NaCl and RTIL. The experimental results were analyzed to determine the dielectric response and changes due to Zn oxidation within the Zn-rich system.

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1. Introduction

We are always interested in expanding the range of usefulness of our electrochemical measurements on corrosion protective organic coatings because such measurements have been one of the best sources on \textit{quantitative} data on such coatings. Water is a major contributor to the ultimate failure of coatings in outdoor and immersion exposure, and thus to limit our electrochemical characterization of coatings to methods that required the use of aqueous electrolytes implied that we were simultaneously negatively affecting our coating system as we made our electrochemical measurements on the coating. To free ourselves from...
this constraint, we initiated a project on the use of RTIL’s in the electrochemical characterization of organic coatings as part of our studies of coating systems. Lt. Col. Paul Trulove, our AFOSR program manager at the time of our initial RTIL effort, worked in this area of materials research [5] and provided encouragement, sources of sample RTIL’s, and preliminary technical advice in considering this new and exciting class of liquids [6] in our studies of coatings. As noted in the electrochemical literature on this new class of liquids, there is much yet we do not understand, for example, the structure of the double layer in such materials [7].

The degree to which water can intrude on measurements of coating materials is very significant, but not often recognized. Consider the use of electrochemical (EC) measurement techniques for organic coatings, the subject of AETOC 07 [8]. All of these techniques mainly depend on the use of aqueous electrolytes. We are largely concerned with using these techniques to measure the corrosion protective properties of coatings. But, aqueous electrolytes affect the polymers used in corrosion protective coatings—water intrudes on the measurements. Further, water dissolves in many of the polymers used in protective coatings. The water uptake of epoxy-based polymers commonly used in organic coatings may be approximately 6% by volume and in polyurethanes, may be about 2% by volume [9]. This water uptake plasticizes coatings based on such polymers, and the thermal and transport properties of such systems are severely altered. In addition, the dielectric constant of water (∼80) is much larger than most dry polymers (∼5) used in coatings. This make the characterization of drying stage of wet–dry cycling in regular or accelerated exposure by EC techniques based on aqueous electrolytes largely unfeasible. This has been true in trying to acquire baseline data on organic coatings before outdoor or accelerated exposure. Such data are not often sought nor acquired because short periods of immersion are inaccessible in the low-frequency regions of EIS often used to analyze the coatings. Also, measurement of non-steady-state situations in coatings not pursued very often – most often “steady state” results are sought and desired throughout measurements. This means that when a coating is not saturated with water, multiple frequency EIS spectra are inaccessible because the measurement requires stationarity at each frequency. The low-frequency portions of the standard EIS spectra are definitely changing (non-stationary) within the time scale of diffusion of water into the organic coating, so cannot be used in analyzing dynamic wet–dry cycling processes.

2. Initial studies

The initial goal of the study was to identify and then utilize as a non-aqueous conductive liquid RTIL’s with which we could do an electrochemical measurement such as EIS on coating films without the effects of aqueous electrolyte diffusing into the film. The RTIL we initially utilized was 1-butyl-1-methylpyridinium trifluoromethane-sulfonate (C10H22N+SO3F–RTIL-A) and water (for size comparison).

By this relatively simple use of a hydrophilic RTIL in our electrochemical measurements, we expanded considerably our measurement capabilities with respect to water transport in coatings.

3. Modeling and measuring water content in coatings

From our initial studies we now had a technique that would enable us to make measurement of the capacitance of a coating during drying as the egress of water due to its migration from the coating to the hydrophilic RTIL as well as the ingress of water into a coating during immersion in an aqueous electrolyte. Since penetration of water and ions is a major cause for loss of barrier properties and constitutes the first step to coating delamination and underfilm corrosion, the determination of the water content in a coating is thus a parameter of relevance for corrosion scientists and has been studied extensively [12–19]. In a constant frequency EIS measurement during wetting and drying, we have available to us a continual measurement of the capacitance of an organic coating, C:

\[ C = \frac{\varepsilon_0 \varepsilon A}{h} \]

where \( \varepsilon \): relative dielectric constant; \( \varepsilon_0 \): permittivity of vacuum; \( A \): area of the sample and \( h \): coating thickness.

With this capability to measure directly and continually the capacitance of a coating through wetting and drying cycles comes the capability of following the concentration of water in a coating. There is an extensive literature on inferring the amount of
water in coatings and polymers from measurement of the dielectric constant of the system and many models have been proposed for doing this. Since the dielectric constant of a polymer is typically one order of magnitude lower than that of water, water absorption leads to a global increase of $\varepsilon$, thus leading to a rise of the measured capacitance. All these models are based upon the measurement of a capacitance, usually by electrochemical impedance. In order to make measurements that refer to the whole coating, the experimental arrangement requires the presence of an ionic liquid as a function of time, using the hydrophilic RTIL as the measurement medium.

Brasher and Kingsbury [12] were the first to make use of effective medium theory equations for estimating the dielectric constant of mixed materials and proposed a model for the estimation of the instantaneous water volume fraction in an organic coating, $\phi(t)$:

$$\phi(t) = \frac{K \log(C(t)/C_0)}{\log(\varepsilon_w)}$$

where $C(t)$: capacitance at time $t$; $C_0$: capacitance of the dry coating (usually obtained from extrapolation to $t = 0$ in continuous immersion experiments), $\varepsilon_w$: dielectric constant of water ($\varepsilon_w = 80$ at $25^\circ$C) and $K$ is a measure of the swelling of the coating ($K = 1$ if there is no swelling).

Several other models can be found in the literature for mixed dielectric constants, but none of them has lead to alternative useful models for water in polymers. Lindqvist [20] presented a revision and comparison of the various models for mixed dielectric constants and concluded that Eq. (4) was the one that led to best results. Sykes [21] proposed a variant for the equation, but the estimates do not seem to improve the results. Recently, a model based upon linear combination of dielectric constants was proposed by Castela and Simoes [22] and shown to give results closer to those from other techniques:

$$\phi(t) = \frac{C(t) - C_0}{C_{sol}}$$

where $C_{sol}$ is the capacitance of a layer of water with the same dimensions as the coating.

Further, the use of an RTIL before the coating had any contact with water or aqueous electrolyte solution enabled us to secure an electrochemical characterization of the coating in its true "original" state and gives us a baseline value of the coating system electrochemical properties to use in evaluating system changes upon exposure.

4. Examining wet–dry cycling effects in coatings using RTIL’s

To pursue the new capability for examining electrochemically both drying and soaking of organic coatings, we used the single frequency EIS measurement method (usually performed at $10^4$ Hz) to acquire data during the drying and wetting for a non-pigmented epoxy coating over Al 2024 at various temperatures of measurement. There are new features to the EIS plot signatures that we have not yet fully interpreted, but beyond a doubt, we now have a new tool for characterization of coatings. A detailed description of this work is given in a recent paper [2].

Metallic structures covered with a protective organic coating must provide corrosion protection to outdoor conditions that include cyclic wetting and drying conditions. In past work in this laboratory, we have pointed out that this type of cyclic exposure eventually causes sufficient damage to the coating to make a large contribution to the failure of that coating [10]. The measurements of the water absorption and desorption for a coating under cyclic wet–dry conditions by gravimetry [20] and capacitance changes have been reported [18,23] in past studies. In these reports the wetting stage involved immersion in an aqueous electrolyte and the drying stage involved exposure to air. The drying stage of a wet–dry cyclic experiment has been reported to be simulated by immersion in a hydrophilic room temperature ionic liquid (RTIL). The capacitance evolutions associated with the wet and dry stages were calculated from single frequency impedance responses. The diffusion coefficients associated with the soaking and drying stages were reported as $8.0 \times 10^{-14}$ m$^2$ s$^{-1}$ and $1.9 \times 10^{-14}$ m$^2$ s$^{-1}$, respectively for the epoxy coating under study.

Results associated with an experimental procedure employing cyclic 0.05 M NaCl soaking and RTIL drying conducted on samples of epoxy coating on AA 2024-T3 are presented and discussed. A control experiment was also conducted where a natural drying stage was used, by exposure to air in a desiccator, instead of the RTIL drying
stage. The capacitance data obtained from these experiments were analyzed using models to determine the values of \( D_{\text{in}} \) and \( D_{\text{out}} \). Experiments were also conducted where EIS spectra were obtained for the samples under constant immersion in 0.05 M NaCl and RTIL. The data from these experiments were used to compare wet–dry cycling with constant immersion, and to determine whether the use of RTILs were suitable for simulating drying conditions.

The use of RTILs as a medium to monitor the drying process of an organic coating is novel. However, a limitation to the approach is the possible influence of the RTIL on the electrochemical properties of the coating. Current results demonstrate that the RTIL did not influence the coating properties under constant immersion but may have done so after several electrolyte immersion–RTIL dry cycles. This will be addressed by using an RTIL with larger ions such that entry into the coating by diffusion or through pores would be reduced.

Experiments were conducted using the experiment set up schematically shown in Fig. 3 to characterize the response of an epoxy coating to cyclic wetting and drying stages. Continuous immersion for approximately 24 h in a 0.05 M NaCl medium represented the wetting stage. Two drying stages were used: (1) a natural drying stage where the coated panel was placed in a desiccator with the cylinder and O-ring removed and (2) a simulated RTIL drying stage where the test area was exposed to the hydrophilic RTIL 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate \((\text{C}_{10}\text{H}_{20}\text{F}_{3}\text{NO}_{3}\text{S})\). The thickness of the epoxy coatings used in the cyclic wetting–RTIL drying and cyclic wetting–natural drying were 32 ± 4 and 42 ± 5, respectively, which represented the average of 13 individual measurements of the thickness of the area of the sample to be exposed to immersion.

The wetting stage involved exposing the sample area to an immersion of 0.05 M NaCl for approximately 24 h during which the impedance at a single frequency of 10 kHz was measured to monitor the changes in the coating. After the wetting stage the glass cylinder and O-ring were removed. For samples in which the drying stage was monitored, a cylinder and O-ring was clamped exposing the same sample area as was under immersion in the wetting stage. The sample area was immersed in the RTIL using a clean counter electrode for approximately 24 h during which the impedance at a single frequency of 10 kHz was measured to monitor the drying process. Following the 24 h period, the RTIL cylinder and O-ring were removed with the sample area then ready for the wetting stage of the following. RTIL electrolytes were replaced with pristine RTIL every three cycles to avoid using saturating the RTIL with water.

The wetting stage for samples undergoing the cyclic wetting–natural drying experiment was as described in the preceding paragraph. The drying stage involved removing the cylinder and O-ring and storing the sample in a desiccator for 24 h. There was no monitoring of the drying stage in this experiment because of the lack of an electrochemical contact.

The data from this study and all others on the use of RTIL’s in our lab has analyzed and interpreted using standard diffusion analysis methods to examine the transport of water into and out of organic coatings. The basic analysis equations one uses are as follows:

The diffusion of water into an organic coating is based on the solution of the Fick’s second law

\[
\frac{\partial c(z, t)}{\partial t} = D \frac{\partial^2 c(z, t)}{\partial z^2}
\]  

where \( c \) and \( D \) are the concentration and diffusion coefficient of water, respectively [3]. The position measured from a reference point, \( z \), and the time \( t \) were the independent variables. A form of the solution of Eq. (6) is given as

\[
M(t) = M_s - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left( -\frac{(2n+1)^2 D \pi^2 t}{4L^2} \right)
\]

where \( L \) is the coating thickness and \( M(t) \) and \( M_s \) represent the mass of water absorbed at time \( t \) and at saturation, respectively [2,8]. This solution is based on the assumption that \( D \) is independent of \( c \) is used in constructing this solution and the solution is applicable to a system absorbing water as well as desorbing water [8]. The ratio of \( M(t) \) to \( M_s \) in Eq. (2) represents the degree of saturation of the coating. An approximate solution [15] to Eq. (2) applicable for short times involves replacing the summation by an integration to yield

\[
\frac{M(t)}{M_s} = \sqrt{\frac{4Dt}{\pi L^2}}
\]

and is applicable for short times.

The volume fraction of an organic coating that is occupied by water \( \phi(t) \) at a time \( t \) is best estimated by Eq. (4) with \( K = 1 \). The degree of saturation of the coating can also be expressed by the ratio of volume fraction at time \( t \) to that at saturation \( \phi_s \) and is given by

\[
\frac{\phi(t)}{\phi_s} = \frac{\log(C(t)/C_0)}{\log(C_s/C_0)}
\]

where \( C_s \) represent the coating capacitance at saturation [1,2].

Combining of Eqs. (8) and (9) yields the expression

\[
\frac{\log(C(t)/C_0)}{\log(C_s/C_0)} = \sqrt{\frac{4Dt}{\pi L^2}}
\]

that can be used to calculate value of \( D \) from capacitance measurements under the assumption of the short-time approximation. The capacitance data associated with the wetting and drying stages of nine cycles for the epoxy are shown in Fig. 4. As expected the capacitance increased during immersion in the aqueous 0.05 M NaCl as
the water uptake by the coating increased the effective dielectric property of the coating. During immersion in the RTIL the capacitance decreased as the water removal by the hydrophilic RTIL property of the coating. During immersion in the RTIL the capacitance decreased as the water uptake by the coating increased the effective dielectric property of the coating.

The data shown in Fig. 4 is the first such data acquired, to our knowledge, and thus there are many unexplained features to the data. The data present in Fig. 4 is for one sample of coating only, and is given as a demonstration of concept for the use of RTIL’s in coating cycling studies. We are planning experiments to document the reproducibility of such data by examining the reproducibility in the measured diffusion coefficients and other parameters that are intensive (not film thickness dependent) measures of the system. For example, the over-shoot of the C(t) data from the saturated value at steady state shown in the water up-take measurements. The overshoot is maximum in the initial measurement, and then it decreases as cycling progresses. One may attribute this to possible crystallinity or other structural artifacts of the film formation process that are annealed from the polymeric coating during cycling. It is known that polymers can show “memory” and this may also indicate formation of preferred pathways of ingress and egress for water molecules from the coating. We are examining these types of artifacts in our data record to determine what other properties of the coating can be studied by this methodology.

The measurements show breaks in the data between wetting and drying caused by the time it takes to change the sample form one immersion solvent (water + electrolyte) to another (the RTIL) in our experimental procedure. This is currently unavoidable, but will be minimized as these measurements are repeated further.

The capacitance evolution for the wetting and drying stages as shown in Fig. 5 as a function of the square root of time (t^0.5). An initial linear trend followed by the asymptotic approach to a steady value indicated that the wetting and drying processes were consistent with Fick’s second law for most of the stages. An evolution not consistent with Fick’s second law was the wetting stage of cycle 1 where the maximum capacitance was not associated with the saturated condition. The drying stages indicated by 3.5, 4.5 and 5.5 for cycles 3, 4 and 5, respectively had an anomalous behavior where there was an observed increase in the capacitance after the linear decrease which was followed by the asymptotic decrease to a steady value.

As discussed above in conjunction with Fig. 4, it is uncertain what causes the non-monotonic behavior with time of C(t) in the wetting and drying cycles. The deviation from monotonicity occurs to the largest extent in the early cycles of wetting and drying, and what may be observed is the relaxation of the polymer to a steady state configuration. If one examines the literature of coatings studies by EIS, most authors throw away the early data (from initial immersion, for example) as non-stationary, not following the KK relationships, and full of polymer related artifacts. As our data was acquired at high frequency, and thus at a much more rapid rate than the rate of polymer rearrangements, it is from a “stationary” physical situation, and thus shows changes never carefully observed previously. We are currently trying to interpret this data in detail.

The values of the diffusion coefficient associated with the wetting and drying stages of the epoxy coating exposed to the cyclic 0.05 M NaCl immersion and RTIL drying are shown in Fig. 6. These values were calculated using Eq. (10). Given in Fig. 6 are the diffusion coefficient values for the coating associated with the wetting by 0.05 M NaCl and the drying in the desiccator. These results illustrate that wetting and drying are not symmetric processes, as the saturated coating will have effectively a larger diffusion coefficient because of plasticization of the polymer by water. The local drying of the interface during RTIL/drying step immersion will lower the global diffusion coefficient as measured on the total system.

We now have a considerable effort examining wet–dry cycling of various types of coatings using sequential immersion in aqueous electrolyte then in RTIL as the “wet–dry” cycle, and are gaining insight into the way water goes in an out of coatings during exposure. Our very first set of measurements on this phenomena showed that the diffusion process was not symmetric, i.e., the diffusion coefficient for water ingress is different from water egress from the coating [1]. We have also found this to be true in other more recent studies [2,24]. This is shown in more detail in Figs. 7 and 8 for a two-layer urethane/epoxy/Al 2024 T3 system. In all cases, the diffusion coefficient for the water ingress is somewhat larger than that for the water egress (into the RTIL). Fig. 8 indicates the kinetics of the process is non-symmetric throughout the wet–dry cycle. It appears that as water leaves the polymer, the resistance to transport
is higher than when it enters the polymer. Further complicating this data is the fact that this is a two-layer system, and there may be a net accumulation at the interface between the two layers or a diffusional resistance term that must be assigned to the layer 1/layer 2 interface.

What is happening to cause the rates of water ingress (soaking cycle) and water egress (drying cycle) to be somewhat different? Data may need to be reanalyzed using the form of Fick’s second law where the diffusion coefficient is a function of diffusant concentration,

$$\frac{\partial c(z, t)}{\partial t} = \frac{\partial}{\partial z} \left[ D(c) \frac{\partial c(z, t)}{\partial z} \right]$$

or by numerical methods that account for polymer swelling by the diffusant [25,26]. $D(c)$ increases with increasing concentration/ingress of water since water plasticizes the polymer increasing $D$, giving an auto-accelerating diffusion process up to the point of polymer matrix saturation. This as due to the fact that water is a partial solvent/plasticizer for the coatings we have studied, especially the epoxy-based materials, and this gives a non-linear dependence of the process on the diffusion coefficient. The volume of the coating just in contact with the aqueous immersion electrolyte is saturated and swollen. When the hydrophilic RTIL is put in contact with the coating, the coating layer nearest the RTIL is locally dried, and its $D$ decreases, slowing water egress. This dissolved water swells this polymer, and drying the surface region by the RTIL will locally remove the water from the surface layer, locally reducing the plasticization and swelling and thus the total water transport. The water leaving the coating has a decreased effective diffusion coefficient from the polymer relative to the water entering the polymer coating. A similar set of observations of absorption–desorption cycling of liquids into polymers was made by Koenig in an NMR imaging study of the cycling of PMMA rod. This author gave a very similar interpretation of the results to the one given above [27].

5. Thermal cycling of organic coatings in ionic liquids

Former studies in this laboratory have indicated the value of making electrochemical measurements on organic coatings in immersion while the system is undergoing thermal cycling. This method was first described in detail at the first AETOC meeting [28]. It has since proven to be very useful both in our laboratory and in other laboratories studying corrosion protective coatings [29,30]. Because of the unique information provided by such testing, we decided to include such cycling into our studies with RTILs. These studies were recently described in detail [4]. As in previous studies, the properties of the coating under study were characterized as they were heated in immersion, and then again as they were cooled to room temperature ($25^\circ C$). The new part of the experimental examination of thermal effects on coatings was that the drying cycle was performed using the RTIL.

The diffusion coefficient of water in the coating during thermal cycling was determined as described earlier [2]. The diffusion coefficient is plotted during thermal cycling in Fig. 9. The diffusion coefficient is plotted as water goes into the coating, black squares, and as RTIL removes water from the coating, grey squares. At each temperature, the diffusion coefficient is reproducible for the three cycles, though the $D$ for water removal is always less than $D$ for water uptake at the same temperature. Between the thermal cycling steps the coating system is returned to room temperature and single frequency spectra along with occasional complete frequency spectra are taken. These show whether the temperature cycle introduced nonrecoverable changes to the bulk coating properties.
A possible cause for higher capacitance as water is removed at temperatures above room temperature is the RTIL may diffuse into the epoxy. The relative dielectric constant of the RTIL is 24 compared to 80 for unbound water. The diffusion coefficient at room temperature drops after high temperature cycles. A possible mechanism is with water as a plasticizer during cycling, there is annealing in the coating which densifies the epoxy (often referred to as physical aging). As water volume fractions in the epoxy increase, so does the connectivity of the water inclusions. The capacitance, for the same volume fraction of water, increases and drying (RTIL) such as the full frequency EIS spectra, including the modulus $|Z(\omega)|$ and phase angle $\theta(\omega)$ as shown in Fig. 11(a) and (b), respectively. These data are for an epoxy coating whose dry glass transition temperature is 65 $^\circ$C. These plots for the last of the three cycles at each temperature show that there is a clear trend for the modulus of impedance, with the modulus increasing with increasing temperature. The phase angle for RTIL (drying) and aqueous measurements (wetting) start very close, then as the cycles and temperature increase the phase angle separates between aqueous and RTIL electrolytes. The Bode and phase-angle plots show that during the last cycle of 70 $^\circ$C there is a change in behavior; in the low-frequency regime (<frequency 10 Hz) the Bode and phase-angle plots separate. For all temperatures 50 $^\circ$C and below, the Bode and phase angle for water and RTIL are nearly identical. The change begins to be evident in the phase-angle plot on the

$$D(T) = D_0 \exp \left(-\frac{E_A}{RT}\right).$$

where $D_0$ is the diffusion coefficient at some reference temperature $T_0$, $E_A$ is the activation energy for diffusion process and $R$ is the ideal gas constant [32,33]. The activation energy over the gas constant, $E_A/R$, for water diffusion measured in the epoxy is 4000 K$^{-1}$, as determined from TGA and EIS measurements for water ingress. This activation energy is consistent with published values for similar systems for example, $E_A/R$ for diffusion was 4500 ± 100 K$^{-1}$ (3.7 ± 0.1 × 10^4 J [34] for diffusion in an epoxide-phenol using 3% (w/w) NaCl solution for multiple samples. Also, $E_A/R$ for diffusion was determined for an epoxy adhesive as $6700 ± 200$ K$^{-1}$ (5.6 ± 0.2 × 10^4 J [35]. The activation energy for diffusion of water estimated from our data in the coatings appears to show Arrhenius behavior and the activation energy calculated from such behavior is consistent with previously published values. One can extract further information about the coating by being able to monitor electrochemical processes during both soaking (aqueous electrolyte) and drying (RTIL) such as the full frequency EIS spectra, including the modulus $|Z(\omega)|$ and phase angle $\theta(\omega)$ as shown in Fig. 11(a) and (b), respectively. These data are for an epoxy coating whose dry glass transition temperature is 65 $^\circ$C. These plots for the last of the three cycles at each temperature show that there is a clear trend for the modulus of impedance, with the modulus increasing with increasing temperature. The phase angle for RTIL (drying) and aqueous measurements (wetting) start very close, then as the cycles and temperature increase the phase angle separates between aqueous and RTIL electrolytes. The Bode and phase-angle plots show that during the last cycle of 70 $^\circ$C there is a change in behavior; in the low-frequency regime (<frequency 10 Hz) the Bode and phase-angle plots separate. For all temperatures 50 $^\circ$C and below, the Bode and phase angle for water and RTIL are nearly identical. The change begins to be evident in the phase-angle plot on the
last cycle of 50 °C. The phase behavior changes between the water ingress and water egress. This phase-angle difference is even more pronounced on the last cycle of 70 °C. The deviation between the system response as water goes into the epoxy and when the epoxy is exposed to the hydrophilic RTIL, resulting in water removal, is evident.

We are examining our data to determine whether there is any RTIL entry into the coating film, as this also might account for the lack of symmetry in the wetting and drying processes. If the RTIL enters the coating matrix, it will affect the coating matrix differently than the water, especially in terms of plasticization and thermal response.

5.1. Use of RTIL’s in characterizing metal-rich coatings

This use of RTIL’s was motivated by our laboratory’s interest in developing an improved understanding of metal rich-systems due to our success in developing Mg-rich systems for the chromate free protection of Al [36]. [Recent work at NDSU indicates Mg-rich coatings can provide similar protection to aerospace Al alloys such as AA 2024 T-3.] This is the first Cr-free protection system that gives long term protection to such alloys [37]. Metal-rich coatings provide a unique manner of protecting metal substrates. This type of coating is a high volume fraction of metal pigment particles (near the critical pigment volume concentration CPVC) dispersed in non-conductive polymer or inorganic matrix. The pigmentary metal is more reactive than metal substrate to be protected. As particle volume fraction is high enough to give almost complete particle-to-particle contact, when coating is applied to metal substrate it provides sacrificial/cathodic protection to substrate. These coatings were originally designed in late 1930s with particulate Zn to protect steel. Zn-rich coatings act like a galvanizing layer. Design of such coatings has not changed since and little basic research performed on them since then [38].

Metal-rich coatings are most often used as a primer, with a decorative or functional top-coat which provides mainly barrier protection. Such systems need further characterization in their transport properties. One can make the general statement that metal-rich coatings need basic material research to enhance design and function. There has been very little data acquisition and analysis focused on water or electrolyte transport within such coatings during exposure or accelerated testing. Little has been done to acquire proper time series data for lifetime/durability prediction of this class of primers.

However, as the first type of metal-rich coatings, Zn-rich coatings have received the most study of this class of coatings [39–41]. Our initial work was utilizing an RTIL on Zn-rich coatings was the characterization of an Zn-rich primer at various Zn pigment volume concentrations (PVCs) without a topcoat. Again, the point must be made that his in preliminary data, the major point of which is to demonstrate that the use of RTILs in examining coating systems adds a considerable amount of information to a set of experiments relative to similar experiments run only with an aqueous electrolyte. The samples were alternately immersed in a 0.05 M NaCl electrolyte solution and in the hydrophilic RTIL 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate (C10H20F3NO3S). In this set of experiments, we sought to determine the effect of Zn PVC in wet–dry cycling exposure behavior of this primer, and to determine what new information could be gained from the use of the RTIL + electro-chemical characterization during such exposure. The results discussed here are only preliminary and the interpretations of the data proposed are tentative, subject to change as we continue to learn more about the system.

The initial capacitance results on coatings of 5, 15, 25, 45 and 65% PVC are shown in Fig. 12. As Fig. 12 shows, the data is quite complex. One can observe that the 5% and 15% PVC primers seem to be acting like pure barrier coatings, with reversible water transport in and out of the films. The other higher PVC coatings are acting irreversibly in water uptake and may be showing the formation of hydrated zinc oxides and oxychlorides that are typical of this class of coatings. This hydration and dehydration of these oxides may be the primary cause of the behavior of the system after the first full wetting and drying cycle. This will be experimentally determined in future measurements.

With respect to Zn-rich systems, we have demonstrated that single frequency electrochemical impedance spectroscopy (EIS) measurements of impedance as a function of time for Zn-rich primers, or other active systems, gives new data on the evolution of the coating properties. The use of an RTIL allows the improved monitoring of impedance behavior during water egress. Data indicates that this is a very fruitful methodology for the study of these important systems and can offer unique insights into how and why they function. Materials re-design based on this data is already in the planning stage.
5.2. Conclusions and summary

Again, a new technique of materials science was applied to the science of coatings with extremely interesting and important results. RTIL's have proven very useful in characterization of coatings and suggest that their use can assist coating scientists. RTIL's allow characterization of coatings in drying unavailable by previous methods. Continuous EIS monitoring at single frequency gives a dynamic picture of processes occurring in coating exposure and field use. They offer new insight into dielectric effects in coatings, especially transport effects. Data from systems now available are:

- Capacitance of coating during drying as well as drying cycles;
- Volume fraction of water vs. time in coatings;
- Insight into effects of conductive pathways in coatings;
- Diffusion coefficients for water in wetting as well as drying.

All of these data increase our knowledge of water liquid transport in organic coatings. This data allows improved quantitative characterization of metal-rich coatings, and hopefully improved design of this class of coatings.

RTILs offer the option of electrochemical measurements without direct alteration of the samples by ingress of water into the samples. Hydrophilic ILs can be used to examine water egress from organic coatings, something not previously available with standard measurement practice. RTIL use expands the range of EIS and ENM into drying as well as soaking processes. However, open circuit potential (OCP) measurements that have proved so valuable in studying metal rich coatings need to be reconsidered with the use of non-aqueous solvents. The concept of the reference electrode as developed for aqueous electrochemistry is no longer valid in RTILs.

5.3. Future work

In future studies using RTILs with organic coatings, we intend to examine a range of RTIL’s of different sizes and chemical composition. We will vary their molecular size to determine size range at which they begin to penetrate the coating film as well as varying their hydrophilic/hydrophobic nature. We also intend to consider their use as fluids for casting/electrodeposition of conductive polymers, and to examine their use to characterize water-free dielectric properties of organic coatings. We will further use these results in our modeling of coating behavior, and to achieve better understanding of metal particle packing, connectivity, percolation, and related effects in metal-rich coating films.

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