



Use of Ionic Liquids for the Electrochemical Characterization of Water Transport in Organic Coatings

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The growth of the capacitance of organic coatings during immersion in aqueous solutions can be monitored by electrochemical impedance and has long been associated with the inward diffusion of water. For the drying stage, however, the absence of a liquid conducting medium has inhibited the application of the classical impedance methods. This work presents a novel approach, in which an ionic liquid is used as conducting medium to allow the coating to dry while the process is followed by single frequency impedance measurements. The diffusion coefficients for the water ingress and egress were determined.

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Organic coatings protect metallic substrates from corrosion by both inhibition and barrier effects. The barrier effect depends on the adhesion to the substrate but also on the dielectric properties of the film. 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. Determination of the water content in a coating is thus a parameter of relevance for corrosion scientists and has been the subject of many studies.¹⁻⁸ An important parameter for this purpose is the coating capacitance. The approximation of a parallel plate capacitor is usually applied to the capacitance of an organic coating, C , according to the fundamental equation

$$C = \varepsilon \varepsilon_0 A / d \quad [1]$$

where ε is the dielectric constant, ε_0 is the permittivity of vacuum, A is the area of the sample, and d is the coating thickness.

Because 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 ε , thus leading to a rise of the measured capacitance. In the middle of the 20th century, Brasher and Kingsbury¹ made use of equations for predicting the dielectric constant of mixed materials and proposed a model for the estimation of the instantaneous water volume fraction in a coating, ϕ

$$\phi = \frac{K \log\left(\frac{C_t}{C_0}\right)}{\log \varepsilon_w} \quad [2]$$

where C_t is the capacitance at instant t , C_0 is the capacitance of the dry coating (usually obtained from extrapolation to $t = 0$ in continuous immersion experiments), ε_w is the dielectric constant of water ($\varepsilon_w = 80$ at 25°C), and K accounts for 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 led to alternative useful models applied to polymers. Lindqvist⁹ presented a revision and comparison of the various models for mixed dielectric constants and concluded that Eq. 2 was the one that led to best results. Sykes¹⁰ 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 Castela¹¹ and shown to give results closer to those from other techniques

$$\phi = \frac{C_t - C_0}{C_{sol}} \quad [3]$$

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

All these models are based upon the measurement of a capacitance, usually by electrochemical impedance. To make measurements that refer to the whole coating, the experimental arrangement requires the presence of an ionically conductive medium, usually consisting of an aqueous solution with some salt to make it ionically conductive. The advent of room-temperature ionic liquids (RTIL), however, presents new possibilities in terms of electrochemistry. These are salts that are in the liquid state at room temperature and their ionic nature makes them conductive, an essential property in electrochemistry. Furthermore, if a dry ionic liquid is put in contact with an organic coating, there should in principle be a flow of water from the coating to the outer medium, at least if the ionic liquid is hydrophilic. Under these conditions, it should be possible to assess in situ the decrease in the water content as a function of time, using a liquid medium. The results reported here consist of monitoring of the water content in an epoxy clear coat during the process of water uptake (in NaCl aqueous solution) and of subsequent drying (in an ionic liquid) and consist of the preliminary data from a study in progress. To our knowledge, this is the first time drying of an organic coating has been observed by liquid impedance measurements.

Estimation of the diffusion coefficient.—The diffusion coefficient can be determined from the time variation of the coating capacitance. Assuming Fickian diffusion, the early stages of water permeation into a coating can be described by the semi-infinite approach

$$\frac{X - X_s}{X_0 - X_s} = \text{erf}(\eta) \quad [4]$$

where X is the concentration, X_s the concentration at the surface (assumed to be the saturation concentration), X_0 the initial concentration (assumed to be constant throughout the coating), erf is the error function, and η is a dimensionless group given by

$$\eta = \frac{x}{\sqrt{4Dt}} \quad [5]$$

where D is the diffusion coefficient, t is the time of immersion, and x is the distance from the outer coating surface. The mass flux of water ingress, M'_s , is then given by

$$M'_s = \frac{D(X_s - X_0)}{\sqrt{\pi Dt}} \quad [6]$$

The total mass of water permeated, M_t , can be obtained by integrating the mass flux over time. The fraction of saturation is given¹² by the ratio between M_t and the total mass of water at saturation, M_∞

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$$\frac{M_t}{M_\infty} = \frac{1}{\sqrt{\pi}} \sqrt{\frac{4Dt}{L^2}} \quad [7]$$

In this equation it is assumed that water ingress occurs only at the outer surface of the coating (coating applied on a substrate) and L represents the total thickness of the coating. The ratio in Eq. 7 thus corresponds to the degree of saturation and is equivalent to the ratio between the volume fraction ϕ and the saturation volume fraction, ϕ_∞ .

$$\frac{M_t}{M_\infty} = \frac{\phi}{\phi_\infty} \quad [8]$$

The relationship between this mass fraction given by Eq. 7 and the capacitance requires one of the equations presented above. Bellucci¹³ used Eq. 2 to derive an equation for small ϕ_∞ that, for only one boundary ingress, is given by

$$\frac{M_t}{M_\infty} = \frac{C_t - C_0}{C_\infty - C_0} = \frac{1}{L} \sqrt{\frac{4Dt}{\pi}} \quad [9]$$

This equation can also be obtained from the model in Eq. 3, and allows the determination of D from the slope of a plot of the capacitance, C_t , vs the square root of time

$$C_t = C_0 + (C_\infty - C_0) \frac{1}{L} \sqrt{\frac{4Dt}{\pi}} \quad [10]$$

If the capacitance C_t is plotted as a function of \sqrt{t} , then the capacitance of the dry coating corresponds to the y-axis intercept of the plot, whereas the diffusion coefficient can be obtained from the slope, provided the capacitance at saturation, C_∞ , is known. The value of C_∞ can be obtained from the flat portion of the curve in an absorption curve, i.e., when the coating becomes saturated after long exposure times, or from the extrapolation to $t \rightarrow 0$ in a desorption curve.

Experimental

The substrate consisted of aluminium panels of AA 2024-T3, supplied by Q Panel Lab products (Cleveland OH). The coating was a nonpigmented epoxy, prepared by mixing a bisphenol-A diglycid ether resin (Epon resin 828-X-95) and the modified polyamide Epikure 3175 curing agent (both from Resolution Performance Products, Houston, TX) in the proportion 65:35, by volume. The solvent was 2-butanone, used in the proportion of 40 vol % of the total tricomponent mixture. The mixture was stirred at room temperature until homogeneity was reached and the application was made using a draw-down bar. Curing was made for 1 h at 90°C followed by 48 h at room temperature. The average dry film thickness was 55 μm .

The electrochemical cell consisted of a glass cylinder clamped on the surface, leaving an exposed area of 7 cm^2 . Impedance measurements were made using a two-electrode arrangement, with a platinum gauze as counter and reference electrode. A Gamry PC4/300 potentiostat/galvanostat with dedicated EIS 300 software (Gamry Instruments Inc.) was used to perform the experiments. Because the system remained highly insulating for a long time, it was decided to perform the experiments at a potential of 0 V between the two electrodes. The measurements were made at a fixed frequency of 10 kHz, with 20 mV amplitude. The electrolytes consisted either of NaCl 0.05 M or of a RTIL (from Merck): 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ($\text{C}_{10}\text{H}_{20}\text{F}_3\text{NO}_3\text{S}$). This ionic liquid is totally miscible with water and was chosen for being hydrophilic.

Results and Discussion

The coating capacitance was determined by computing the angular frequency ω and the imaginary part of impedance Z_i , according to

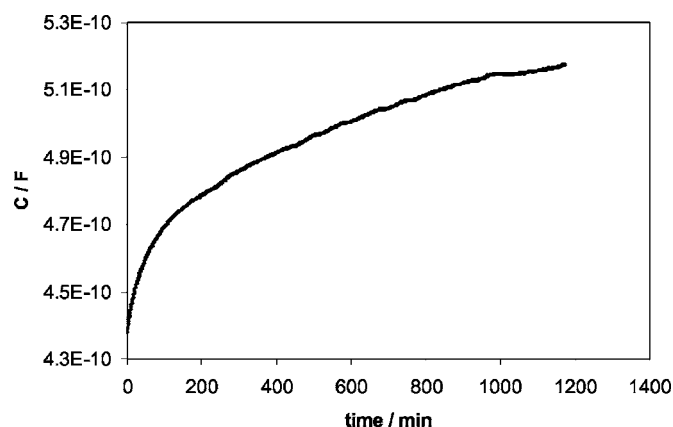


Figure 1. Coating capacitance (10 kHz) evolution during continuous immersion in 0.05 M NaCl.

$$C = \frac{-1}{\omega Z_i} \quad [11]$$

The time evolution of the coating capacitance in the NaCl solution is given in Fig. 1. The evolution is identical to that observed by several authors and, although total stabilization of the capacitance was not achieved, it is clear that it asymptotically approached a saturation value. After the sample was left for 24 h in the salt solution, the solution was removed, the cell and the sample were wiped to remove any excess water and the cell was filled with the ionic liquid. The soaked sample quickly decreased its capacitance (Fig. 2), reaching practically the same capacitance values as observed in the first stages of the soaking process.

Repetition of the soaking/drying cycle revealed a nearly total reversibility, although the capacitance was slightly higher in later cycles, see Fig. 3. This could be due to irreversible opening of the coating polymer structure caused by water ingress, to heterogeneous absorption, which would lead to different degrees of swelling along the surface and therefore to an increased surface area, or to trapping of some of the ions from the solution inside the coating matrix. By using Eq. 10 we estimated the diffusion coefficient from the each of the soaking/drying cycles. For the absorption, the plot of the capacitance vs the square root of time gave practically the same slope in the two cycles, see Fig. 4. The same was observed in the drying stage, see Fig. 5. The values of the capacitance extrapolated to $t = 0$ and the estimated capacitance for $t \rightarrow \infty$, as well as the slopes of the C vs \sqrt{t} plots and the diffusion coefficients are presented in Table I. In this table, $C_{t \rightarrow 0}$ (capacitance at $t = 0$) corresponds to the ca-

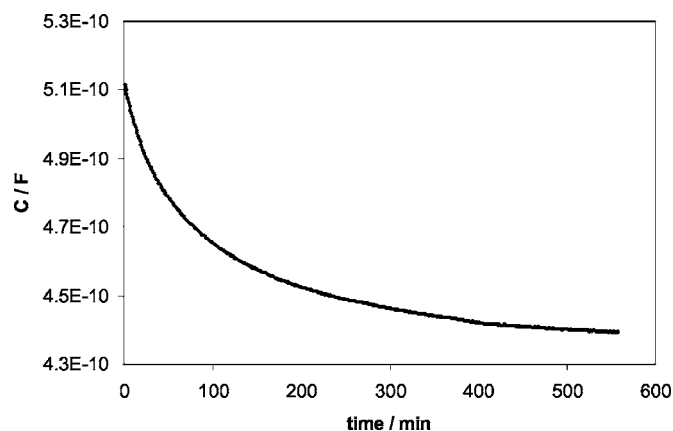


Figure 2. Coating capacitance (10 kHz) evolution of an initially soaked coating during continuous immersion in the ionic liquid.

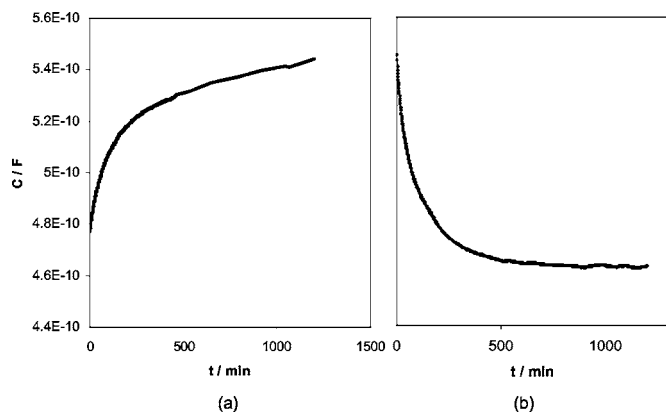


Figure 3. Coating capacitance (10 kHz) evolution in the second soaking + drying cycle. (a) Soaking in NaCl aqueous solution. (b) Drying in the ionic liquid.

capacitance of the dry coating in the case of the soaking stages and to that of the saturated coating for the drying stages, whereas for the $C_{t \rightarrow \infty}$ column the meaning is the opposite. The final capacitance of each stage corresponds approximately to the initial capacitance of the following one, the exception being the transition from the second to the third stage, where a raise in capacitance seems to have occurred in the cleaning stage, when the liquid change was made. The uncertainty presented for the diffusion coefficient is based only upon the errors from the slope and the $C_{t \rightarrow 0}$ extrapolation. It should be noted that the capacitance for $t \rightarrow \infty$ was estimated by taking the values of the last 10 measurements, but only considering the digits down to the picofarad, which eliminates the effect the fluctuations observed and also those expected from the extrapolation of the line to longer times. This estimation has an uncertainty that could affect the estimation of the diffusion coefficient. Nevertheless, the differences in the values of the slopes are well above that effect. The values of D estimated in this way are nearly the same in the two cycles, but they are higher for water diffusing out of the coating compared to water diffusing inwards. These values are in the range expected for diffusion in polymers¹⁴ and are close to the value of

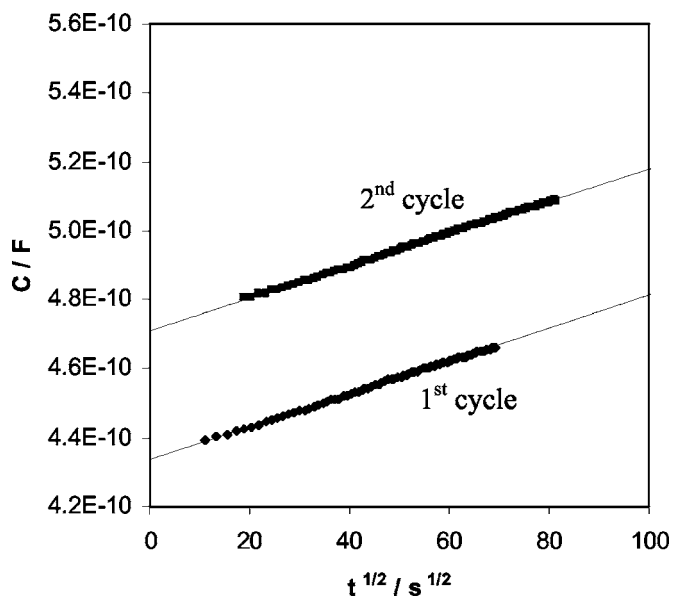


Figure 4. Evolution of the coating capacitance in the first stages of immersion in NaCl solution.

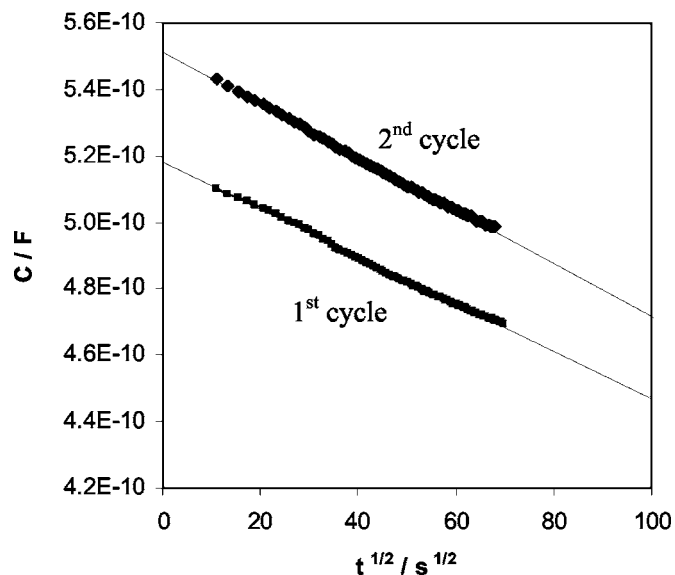


Figure 5. Evolution of the coating capacitance in the first stages of immersion in the ionic liquid.

$D = 2 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ presented by Bellucci¹³ for Kapton free-standing films.

To support our interpretation of the results, a blank experiment was made, in which one sample was dried in the dessicator and then directly immersed in the ionic liquid, without previous immersion in the salt solution. This sample had a lower capacitance, thought to be due to slight dispersion in thickness among different samples. As could be anticipated, there was no growth of the capacitance, see Fig. 6, but rather a very small decrease. This decrease was much smaller than in the other set of tests and can be due to some retention of water even in the dry atmosphere of the dessicator. In fact, the total capacitance variation, estimated as the ratio of the minimum vs. maximum capacitance in each curve, gave 0.97 in the blank test and 0.84-0.85 in all of the other experiments. This means that the coatings dried in the dessicator retained some moisture that diffused out more easily in the ionic liquid than it did in the atmosphere, possibly due to some plasticizing effect of the liquid. Further drying made by heating at 60°C for 1 h finally led to complete absence of water, confirmed by the observation of a constant capacitance when the sample was immersed in the ionic liquid (not presented).

There are two other methods reported in the literature for applying electrochemical techniques to organic coatings without having the counter electrode immersed in an aqueous solution. One of them consists of using a sandwich-type arrangement¹⁵ in which the counter electrode can be either mercury or a solid metal (in this case the coating being cast between the two plates). In this case, not only is the diffusion restricted by geometrical factors or by adhesion, but the drying process can itself lead to the formation of a thin layer of water at the interface and affect the results. The other alternative consists of using embedded metal electrodes.¹⁶ This arrangement, however, uses electrodes with a symmetry that is different to that of the coating and, consequently, the measurements are prone to be determined mostly by the layers of the coating that have lower impedance. The arrangement and procedure now presented have advantages compared to any of those techniques. The mass transport across the outer surface of the coating has the same symmetry as the absorption step and therefore the estimation of the diffusion coefficient is more reliable. Furthermore, the whole setup is simpler and identical to most of the classical impedance measurements and the measurements are made across the total thickness of the coating.

Ionic liquids are a new type of material, or solvent, which very specific properties. Their use is mostly associated with synthesis, but

Table I. Parameters involved in the determination of the diffusion coefficients.

Stage	Solution	$C_{t \rightarrow 0}$ (Farad)	$C_{t \rightarrow \infty}$ (Farad)	Slope ($F s^{-1/2}$)	D ($m^2 s^{-1}$)
1 (soaking)	NaCl 0.05 M	4.34×10^{-10}	5.20×10^{-10}	4.78×10^{-13}	$(7.3 \pm 0.05) \times 10^{-14}$
2 (drying)	RTIL	5.18×10^{-10}	4.39×10^{-10}	-7.15×10^{-13}	$(19.4 \pm 0.20) \times 10^{-14}$
3 (soaking)	NaCl 0.05 M	4.71×10^{-10}	5.52×10^{-10}	4.70×10^{-13}	$(8.0 \pm 0.05) \times 10^{-14}$
4 (drying)	RTIL	5.51×10^{-10}	4.63×10^{-10}	-7.96×10^{-13}	$(19.4 \pm 0.20) \times 10^{-14}$

their good electrical conductivity associated with their solvating power⁷⁷ makes them potentially interesting for many electrochemical applications, the first of them having probably been electrodeposition.¹⁸ Other more recent applications deal with other systems such as batteries¹⁹ or the preparation of capacitors.²⁰ Our search of the literature, however, has not revealed any study with the application of ionic liquids to the variation of the dielectric properties of polymer films. The study now presented shows that it is possible to reversibly change the water content in the polymer by changing the outer liquid medium and it opens new possibilities for the use of ionic liquids in corrosion studies.

Conclusions

The water content in an epoxy clear coat applied on a metal substrate was monitored by the variations in the coating capacitance.

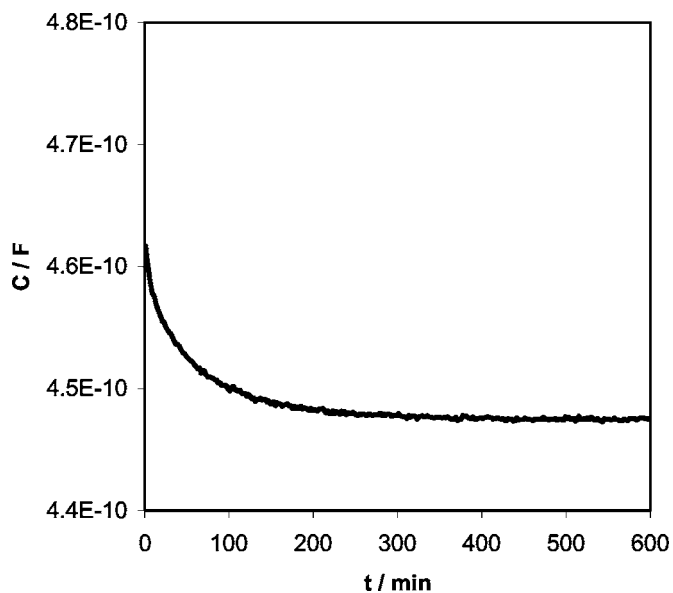


Figure 6. Coating capacitance (10 kHz) evolution of a dessicator-dried sample immersed in the ionic liquid.

Monitoring of the drying process was made possible by the use of a hydrophilic ionic liquid as the conducting medium. The process was near totally reversible and the diffusion coefficients were in the range expected. A slight difference between the diffusion coefficients revealed a faster outward diffusion compared to the inward diffusion.

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