An impedance model for the estimation of water absorption in organic coatings. Part I: A linear dielectric mixture equation

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Abstract

A capacitance model for the estimation of water uptake in polymeric coatings is presented. The model is based upon a linear combination of the individual capacitances of the polymeric phase, the water and the air contained in the coating. Experimental comparison of the model with gravimetric data has revealed an improvement with respect to the classical equations.

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1. Introduction

Electrochemical Impedance has been used by several authors for the determination of the water content in organic coatings [1–11]. The reason for that interest lies on the fact that the capacitance of the coating is sensitive to the penetration of water. Its dependence can be described by the simple model of a dielectric, with a capacitance $C$ that is directly proportional to the relative dielectric constant of the coating and to the area $A$ of the capacitor (in this case the surface area of the coating), and inversely proportional to the coating thickness $d$:

$$ C = \frac{\varepsilon \varepsilon_0 A}{d} $$  (1)

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The constant $\varepsilon_0$ represents the dielectric constant of free space, $(8.854 \times 10^{-14} \text{ F/cm})$. Since the dielectric constant of polymers is typically in the range 3–8, and for water it is 78.3 at 25 °C, then the absorption of water shall lead to a rise in the mixed dielectric constant, resulting in a higher capacitance.

The most used model to estimate the water constant in a coating was proposed in 1954 by Brasher and Kingsbury [1]:

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

In this equation, $C_t$ and $C_0$ represent the capacitance at an instant $t$ and the capacitance of the “dry” coating, respectively, $\varepsilon_w$ is the dielectric constant of water and $\phi$ is the water content, expressed as the volume fraction in the coating. $K$ accounts for the increase of volume, and it should not exceed 1.25. Usually it is taken as $K = 1$, corresponding to constant volume.

Eq. (2) was in fact derived from a formula proposed by Hartshorn et al. [12] for a mixed dielectric constant, $\varepsilon_r$:

$$\varepsilon_r = \frac{(V_{\text{coating}}/V)_{\varepsilon_{\text{water}}}}{(V_{\text{water}}/V)_{\varepsilon_{\text{air}}}}$$

Brasher and Kingsbury observed that their equation gave values higher than gravimetry, and interpreted the discrepancy by a distribution of pores perpendicular to the surface. They also suggested that values lower than reality could be due to a number of situations, such as pores parallel to the surface or the presence of a polar solvent that was pushed by water.

There are several models in the literature to describe the theory of permittivity of heterogeneous materials, although not specifically for paints [2]. For the model of one inner component (water) considered to be uniformly dispersed as spherical particles randomly distributed in an outer continuous medium, then Rayleigh’s equation has been proposed:

$$\frac{\varepsilon_m - \varepsilon_0}{\varepsilon_m + 2\varepsilon_0} = \phi \frac{\varepsilon_i - \varepsilon_0}{\varepsilon_i + 2\varepsilon_0}$$

where $\varepsilon_m$ is the measured permittivity of the specimen, $\varepsilon_i$ is the permittivity of the inner component, $\varepsilon_0$ is the permittivity of the outer continuous medium and $\phi$ is the water volume fraction.

Another approximation, valid for high $\phi$ values, is Boettcher’s mixture formula:

$$\frac{\varepsilon_m - \varepsilon_0}{3\varepsilon_m} = \phi \frac{\varepsilon_i - \varepsilon_0}{2\varepsilon_m + \varepsilon_i}$$

By transforming Rayleigh’s equation, Bruggeman obtained:

$$1 - \phi = \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i - \varepsilon_0} \left( \frac{\varepsilon_0}{\varepsilon_i - \varepsilon_0} \right)^{1/3}$$

Similar to the Rayleigh’s equation is the Wagner’s equation:

$$\frac{\varepsilon_m - \varepsilon_0}{3\varepsilon_0} = \phi \frac{\varepsilon_i - \varepsilon_0}{2\varepsilon_m + \varepsilon_i}$$
A different mixture equation is Looyenga’s equation:

$$\varepsilon_m = \left[ \varepsilon_0^{1/3} + \phi (\varepsilon_1^{1/3} - \varepsilon_0^{1/3}) \right]^3$$  \hspace{1cm} (8)

By using Eq. (1) all these mixtures equation can be written substituting the $$\varepsilon$$ values by the respective capacitances [2].

Lindqvist [2] made an experimental comparison of these mixture equations and concluded that the best approach to gravimetric data was given by the Brasher–Kingsbury equation. However, in many cases even the values from this equation were significantly above those from gravimetry.

More recently, Bellucci and Nicodemo [6] developed two models, the discrete model (DM) and the continuous model (CM), for the determination of the ratio $$\phi/\phi_s$$. In the DM, the film is considered homogeneous and described by a simple RC circuit. For low water contents, and with the use of the Brasher–Kingsbury equation, the reduced water volume fraction comes as

$$\frac{\phi}{\phi_s} = \frac{C_t - C_0}{C_\infty - C_0}$$  \hspace{1cm} (9)

The CM model described the film as a set of individual layers of thickness $$\delta d$$, each of them being homogeneous and described by a RC circuit. The correlation obtained was:

$$\frac{\phi}{\phi_s} = \frac{C_t - C_0}{C_\infty - C_0} \left( \frac{C_\infty}{C_t} \right)$$  \hspace{1cm} (10)

where $$\phi_s$$ represents $$\phi$$ at saturation and $$C_\infty$$ the capacitance at saturation.

This model was used for the determination of diffusion coefficients, but it does not give an absolute value of the water content. Other publications [7,13,14] have dealt with the permeation of water and ions, but not specifically with the determination of the water content.

In spite of the interest and possibilities of the impedance technique for the estimation of the water content in organic coatings, important discrepancies still exist between the models available and reality [15,16]. Part of these discrepancies are certainly related with the calculation of the dielectric constant of a soaked coating. In this work a new model, based upon a linear combination of dielectric constants, is presented.

2. Model development

2.1. Introduction

With the purpose of developing a new model for the estimation of water absorption based on impedance results, the system shall be considered as being composed of the coating as well as the air and the solution contained in it at each instant. Thus, we shall consider:
- Coating—it consists of the solid phase, excluding the air and the humidity trapped inside.
- Solution—solution contained in the coating. Normally it is considered as pure water.
- Film—system formed by the coating, the air and the solution.

Given the previous definitions, it is convenient to state the following simplifying assumptions:

(a) The components in the film are insoluble among them.
(b) The film does not suffer swelling nor contraction during the water absorption process.
(c) The film composition is constant throughout the thickness.
(d) The coating is homogeneous, and therefore its electric parameters are considered constant in all the extension of the coating.
(e) The electrical behaviour of the film can be described by a circuit of RC networks arranged in series, each RC corresponding to one layer of film.

For uniform composition and properties of the film (assumption c and d), the complex circuit of RC networks in series degenerates in the simple circuit [6], as in Fig. 1, of one resistance and one capacitance, $R_f$ and $C_f$, in parallel between them and in series with the solution resistance $R_Ω$.

The impedance $Z$ (expressed in ohm) is then given by

$$Z = R_Ω + \frac{R_f}{1 + j\omega C_f R_f} = R_Ω + \frac{R_f(1 - j\omega C_f R_f)}{1 + (\omega \tau_f)^2}$$  \hspace{1cm} \text{(11)}

where $\omega$ is the angular frequency defined has $\omega = 2\pi f$, in which $f$ is the frequency, and the term $\tau_f = C_f R_f$ represents the time constant of the film.

Since the impedance is given by a complex number of the form $Z_{\text{real}} + jZ_{\text{imag}}$, then the two components are given by

$$\begin{align*}
Z_{\text{real}} &= R_Ω + \frac{R_f}{1 + (\omega \tau_f)^2} \\
Z_{\text{imag}} &= -\frac{\omega C_f (R_f)^2}{1 + (\omega \tau_f)^2}
\end{align*}$$  \hspace{1cm} \text{(11')} 

![Fig. 1. Equivalent circuit for an intact coating.](image-url)
At high frequencies, \((\omega \tau_f)^2 \gg 1\), and consequently the imaginary part of impedance becomes:

\[
Z_{\text{imag}} \approx -\frac{1}{\omega C_f}
\]  

(12)

For a protective organic coating and a reasonably conducting solution, \(R_f \gg R_D\), the high frequency region of the experimental spectrum becomes purely capacitive, with a phase angle of \(\sim 90^\circ\) and \(|Z_{\text{imag}}| \gg |Z_{\text{real}}|\). Therefore,

\[
jZ_{\text{imag}} \approx Z
\]

In the absence of inter-dissolution of the components (coating, water and air), then if a surface parallel to the coating/metal interface is considered, a number of heterogeneities will exist, corresponding to individualized areas for each component. This heterogeneous structure must be similar for all the thickness of the film in a way that the film composition at each layer is the same. Therefore, the film can be divided in parallel elements, since the surface is perpendicular to the current lines, each having the admittance referred to each capacitor component. By this transformation the previous equation leads to the following one:

\[
jZ_{\text{imag}} = -\frac{1}{\omega(C_{\text{coat}} + C_{\text{air}} + C_{\text{sol}})}
\]  

(13)

In this expression the capacitance for each component is present. The evaluation of these capacitances for the film as a whole is not direct, since the solution and air components are present in disconnected zones. However, (see Appendix A) the previous equation can be expressed as

\[
Z_{\text{imag}} = -\frac{-d}{\varepsilon_0 \varepsilon (\varepsilon_{\text{coat}} A_{\text{coat}} + \varepsilon_{\text{air}} A_{\text{air}} + \varepsilon_{\text{sol}} A_{\text{sol}})}
\]  

(13’)

The area occupied by the three components will be expressed as \(A_{\text{coat}}, A_{\text{air}}\) and \(A_{\text{sol}}\). In fact, they correspond to the average of the areas occupied by each component in all the sections.

The area of each component is related with its volume fraction, \(\phi, \phi_{\text{air}}\) and \(\phi_{\text{coat}}\), as follows:

\[
\begin{align*}
A_{\text{sol}} &= \frac{A_{\text{sol}}}{A_{\text{d}}} A = \frac{V_{\text{sol}}}{V} A = \frac{\phi}{\phi} A \\
A_{\text{coat}} &= \frac{A_{\text{coat}}}{A} A = \frac{(A - A_{\text{air}} - A_{\text{sol}})}{A_{\text{d}}} A = \left(1 - \frac{V_{\text{air}}}{V} - \frac{V_{\text{sol}}}{V}\right) A = (1 - \phi_{\text{air}} - \phi) A \\
A_{\text{air}} &= \frac{A_{\text{air}}}{A_{\text{d}}} A = \frac{V_{\text{air}}}{V} A = \phi_{\text{air}} \times A
\end{align*}
\]  

(14)

Substituting Eq. (14) in Eq. (13’) and re-arranging, we get:

\[
\frac{\varepsilon_0 A}{d} \left[\varepsilon_{\text{coat}} + (\varepsilon_{\text{air}} - \varepsilon_{\text{coat}}) \phi_{\text{air}} + (\varepsilon_{\text{sol}} - \varepsilon_{\text{coat}}) \phi\right] = -\frac{1}{\omega Z_{\text{imag}}}
\]  

(15)
For a pure capacitor $C_t = -1/\omega Z_{\text{imag}}$, and the previous expression becomes:

$$C_t = (C_{\text{air}} - C_{\text{coat}})\phi_{\text{air}} + (C_{\text{sol}} - C_{\text{coat}})\phi + C_{\text{coat}}$$  \hspace{1cm} (16)

where $C_{\text{air}}$, $C_{\text{coat}}$ and $C_{\text{sol}}$ symbolize, respectively, the terms $\varepsilon_{\text{air}}\varepsilon_0 A/d$, $\varepsilon_{\text{coat}}\varepsilon_0 A/d$ and $\varepsilon_{\text{sol}}\varepsilon_0 A/d$, and represent the capacitance of uniform layers of air, coating and solution, respectively, with a thickness equal to that of the film. Based on that equation, a relation can be determined for the extrapolated capacitance of the dry coating, $C_0$.

$$C_0 = (C_{\text{air}} - C_{\text{coat}})\phi_{\text{air},0} + (C_{\text{sol}} - C_{\text{coat}})\phi_0 + C_{\text{coat}}$$  \hspace{1cm} (17)

with $\phi_{\text{air},0}$ and $\phi_0$ representing the volume fractions at immersion time for air and solution, respectively. Eq. (16) can also be written for the condition of saturation:

$$C_\infty = (C_{\text{air}} - C_{\text{coat}})\phi_{\text{air},s} + (C_{\text{sol}} - C_{\text{coat}})\phi_s + C_{\text{coat}}$$  \hspace{1cm} (17')

$\phi_{\text{air},s}$ and $\phi_s$ represent the volume fractions at saturation for air and solution, respectively. Subtraction of Eq. (17) from Eq. (16) gives:

$$C_t - C_0 = (C_{\text{air}} - C_{\text{coat}})(\phi_{\text{air}} - \phi_{\text{air},0}) + (C_{\text{sol}} - C_{\text{coat}})(\phi - \phi_0)$$  \hspace{1cm} (18)

The relation between the fractions of the components can be expressed as follows:

$$\phi_{\text{air},s} + \phi_s + \phi_{\text{coat},s} = \phi_{\text{air}} + \phi + \phi_{\text{coat}} = \phi_{\text{air},0} + \phi_0 + \phi_{\text{coat},0} = 1$$  \hspace{1cm} (19)

where $\phi_{\text{coat},0}$ and $\phi_{\text{coat},s}$ represents the volume fraction at the immersion time and at saturation, respectively. From the previous relations we can obtain:

$$(\phi_{\text{air}} - \phi_{\text{air},0}) = (\phi_0 - \phi) + (\phi_{\text{coat},0} - \phi_{\text{coat}})$$  \hspace{1cm} (20)

Using that result in expression (13) the following equation can be obtained:

$$(C_{\text{air}} - C_{\text{coat}})(\phi_0 - \phi) + (C_{\text{air}} - C_{\text{coat}})(\phi_{\text{coat},0} - \phi_{\text{coat}}) + (C_{\text{sol}} - C_{\text{coat}})(\phi - \phi_0) = C_t - C_0$$  \hspace{1cm} (21)

$$\phi_{\text{coat},0} - \phi_{\text{coat}} = C_t - C_0$$  \hspace{1cm} (21')

Based on the assumptions (a) and (d) it can be stated that $\phi_{\text{coat},0} = \phi_{\text{coat}}$. Assuming that initially the film is dry, then the final equation is obtained for the water content in a ternary system consisting of coating, water and air:

$$\phi = \frac{C_t - C_0}{C_{\text{sol}} - C_{\text{air}}}$$  \hspace{1cm} (22)

In this equation, $C_t$ is the measured capacitance (calculated from the imaginary part of impedance) and $C_0$ is obtained from extrapolation of $C_t$ to $t = 0$. $C_{\text{sol}}$ and $C_{\text{air}}$ can be calculated from Eq. (1), taking $\varepsilon_{\text{sol}} \approx 78.3$ and $\varepsilon_{\text{air}} \approx 1$.

A simplification of Eq. (22) can be obtained by considering that $C_{\text{sol}} \gg C_{\text{air}}$:

$$\phi = \frac{C_t - C_0}{C_{\text{sol}}}$$  \hspace{1cm} (22')
The assumption of a binary system (without air), used by some authors, could also be considered. In this case Eq. (17) would become:

\[
Z_{imag} = \frac{-d}{\omega \varepsilon_0 \varepsilon_{coat}(1 - \phi) + \varepsilon_{sol}\phi} A \tag{17''}
\]

Assuming that the moisture in the film at immersion time was zero, then the relation for the water uptake in a binary system can be stated as

\[
\phi = \frac{C_t - C_0}{C_{sol} - C_0} \tag{22''}
\]

Since typically the coating dielectric constant is in the interval \(3 \leq \varepsilon_{coat} \leq 8\), then Eq. (22) would be expected give lower values than expression (22'').

The equations remain dimensionally consistent provided all the capacitance values are expressed in the same units, i.e., either in Farad or referred to the area of the sample (F/cm²).

3. Testing of the model

In order to verify the performance of the model, experimental testing with organic-coated systems was made.

3.1. Experimental

Electrochemical Impedance was made on coated samples and on free films in immersion. Measurements were made using a Frequency Response Analyser (Solartron 1255) coupled to an Electrochemical Interface (Solartron 1286). Measurements were made at ambient temperature in a 3 wt% NaCl solution, except when stated otherwise.

3.1.1. Applied coatings

In order to avoid influence from underfilm corrosion, particularly important in the gravimetry, pure nickel (Goodfellow 99.9%, 0.5 mm) was chosen for substrate in all the tests using applied coatings. The electrochemical cell consisted of a PMMA cylinder glued onto the surface of the panel with epoxy resin. A three-electrode arrangement was used, in which the coated metal was the working electrode. The spectrum acquisition was made in frequency range of 50–10 kHz, with 4–6 points per decade. This was repeated at short time intervals for the first few hours of immersion. The applied wave amplitude was 30 mV and the exposed areas were 10.18 cm². The coatings tested were PVC (200 µm, including acrylic primer), PVDF (25 µm, including polyester primer) and polyester (30 µm, including polyester primer), with a composition kept as simple as possible (here called “model coatings”). The thickness of the primer was always \(\sim 5\) µm. Commercial PVDF coatings of white, black and red colour were also tested.
3.1.2. Freestanding films

Free films were produced without primer to provide low adhesion. The procedure consisted of applying the paint on a clean galvanised steel sheet by a calibrated bar, giving a 200 μm dry film thickness after curing of the paint. The film was cured immediately after the application, in a laboratory convection oven designed for curing of coil coating paints. After the cure the sample sheet was cooled in water and dried. In the absence of the pre-treatment and the primer, detachment was made with minimum stretching of the coating and permanent strain was not observed. The electrochemical tests were made using a two-compartment cell, with the film held vertically between the two compartments. A four-electrode arrangement was used, with a reference electrode and a stainless steel wire electrode in each compartment. Spectrum acquisition was made in frequency range of 166 kHz–1 Hz, with 1 point per decade. The applied wave amplitude was 5 mV and the exposed area was 3.14 cm² on each side of the film. The used film was a commercial PVC, with red pigment. The other coatings (polyester and PVDF) were not tested due to practical difficulties in producing them as freestanding films.

3.1.3. Gravimetry

All weightings were made using a Sartorius MC5 microbalance, working with a resolution of 10 μg. The total weight of Ni-coated samples was in the range 700–800 mg (area of 3.5 cm²) and of the free films, 55–75 mg (5 cm²). Each sample was kept in the desiccator for 3 weeks before immersion. After a fixed period (7 or 21 days) the films were removed from immersion, quickly dried with filter paper, passed in a cold air blow for ≈5 s, and weighted. All the water absorption calculated from the gravimetric data was referred to the final dry weight, due to possible leaching in immersion. The volume fraction of water was calculated as

\[
\phi = \frac{(M_s - M_f)}{\rho_w V_c}
\]

where \(M_f\) and \(M_s\) represent the weight of the coating after drying and at saturation, respectively, \(M_s\) (determined by extrapolation of the drying curve), \(V_c\) is the volume of the coating, calculated from micrometer determinations, and \(\rho_w\) is the specific density of water. The coatings tested were model PVC, model polyester and model PVDF, and white, black and red commercial PVDF, all applied on nickel foils, and also red commercial PVC as freestanding films.

3.2. Results

The various coatings revealed capacitances in the range \(10^{-11}\) to \(4 \times 10^{-10}\) F/cm², which increased during immersion (Fig. 2).

Drying curve for each system after saturation were obtained until a constant weight was achieved. The water volume fraction, determined from Eq. (23), decreased linearly with \(\sqrt{t}\) in a first stage, and then asymptotically approaches zero (Fig. 3). The water fraction at saturation was obtained for each coating as the extrapolation of each of these lines to \(t = 0\).
The capacitance values determined from impedance were converted into water volume fractions by applying the model presented above. Both forms of the model were used, and shall be referred as:

Ternary system equation (TS)—Eq. (22).
Simplified equation (SE)—Eq. (22').

For comparison, the binary system equation (BS)—Eq. (22'')—is also presented.

The water uptake at saturation for PVDF with various pigments applied on nickel foil and compositions is presented in Fig. 4. The maxima and minima in the graph are given by the BK equation and by the gravimetry results, respectively. The gravimetry gave values of $\phi_s$ below 1% under the working conditions, whereas the BK equation gave $\phi_s > 2\%$ in all cases. The $\phi_s$ values given by the model, although higher than the gravimetry values, correspond to 0.4–0.6 of the values from the BK equation. Of the three equations proposed, the highest values were given assuming a binary system, whereas the other two were practically equivalent.

Fig. 5 depicts the time evolution of the water content in three different applied coatings. The dashed horizontal line corresponds to the water content at saturation,
determined from gravimetry. The shape of the absorption curve is similar to the BK equation, and similar to a transient Fickian diffusion. Again the equations of the model give a better agreement with gravimetry, when compared with the BK equation. For the polyester coating the agreement with gravimetry is remarkable, whereas for the PVDF there was some deviation. The PVC coating was the one that was more deviated from gravimetry, although an improvement to the BK model was observed.

Fig. 6 shows the water absorption for PVC freestanding films. Again the BK model presents the highest values, whereas the equation proposed represents a better approach to the gravimetry results.

3.3. Discussion

The estimation of the water content in polymeric coatings is a difficult problem. Commercial coatings are complex systems and there are no models that specifically apply to them. The model that seems closer to reality is that of Brasher and Kingsbury, which is based upon a set of important limiting assumptions:

(a) The capacitance values are related with the coating only, and therefore unaffected by the properties of the outer solution. This assumption is valid provided the solution is conducting.
(b) The increase of capacitance is only due to the ingress of water into the film. This approach is valid provided the film permeability to the ions in solution is low.
(c) The dielectric constant of the water contained in the film is taken as that of the bulk water.
(d) There is no swelling of the film, or else it is taken as being equal to the volume of the water absorbed.
The distribution of water inside the film is uniform. This is of course a rough approximation in conditions of non-saturation. Also, part of the water will tend to penetrate through pores in the coating, and not in a uniform way, leading to a heterogeneous distribution parallel to the surface.

There are no polar solvents in the coating at the instant of immersion.

In theory, the model can thus be applied only to coatings at saturation, with low water contents. Other assumptions can also affect the estimates significantly. For
example, the dielectric constant of the water inside the film is certainly different from that of bulk water.

In our model, the assumptions are basically the same, but we considered the three different components distributed in parallel in each layer, which gave the linear combination of the capacitances.

The model was tested on a limited number of coatings. With the systems tested, the results obtained represent a significant improvement with respect to the estimates made with the same coatings using classical equation. Verification of the model using a wider number of polymers is now necessary in order to establish the real limits of validity of the model.

The model presented above corresponds to a mixture equation that can be expressed as a linear combination of dielectric constants, weighted by the volume fraction of each component:

$$
e_t = \varepsilon_{coat}\phi_{coat} + \varepsilon_{air}\phi_{air} + \varepsilon_{sol}\phi_{sol}$$

This model is mathematically simple when compared to other models presented in the literature. It is known that those models tend to give results excessively high compared to gravimetry. Therefore, it is interesting to compare the equations with the models from the literature.

In conditions of saturation, Eq. (22) will come as

$$\phi_s = \frac{C_\infty - C_0}{C_{sol} - C_{air}}$$

whereas the ratio between Eq. (25) and Eq. (22) gives:

$$\frac{\phi}{\phi_s} = \frac{C_t - C_0}{C_\infty - C_0}$$

Eq. (26) is identical to the one used by Belluci and Nicodemo (Eq. (9)), but it was in fact derived in a different way.
On the other hand, a ratio between the equation of this linear model and the Brasher and Kingsbury equation (BK) gives:

\[
\frac{\phi_{BS}}{\phi_{BK}} = \frac{\varepsilon_t - \varepsilon_{coat}}{\log(\varepsilon_t) - \log(\varepsilon_{coat})} \frac{\log(\varepsilon_w)}{\varepsilon_w - \varepsilon_0}
\]

where \(\phi_{BS}\) (binary system) and \(\phi_{SE}\) (simplified equation) consist of the water uptake calculated by expression (22") and (22'), respectively, \(\phi_{BK}\) corresponds to the water uptake given by the Brasher–Kingsbury equation, and \(\varepsilon_t\) is the dielectric constant of the film at an instant \(t\), obtained using Eq. (1).

**Fig. 7.** Simulation for the ratio between the value of \(\phi\) determined from the linear model and the Brasher–Kingsbury model: (a) Eq. (27) and (b) Eq. (27) (\(\varepsilon_w = 78.3; T = 25^\circ C; \varepsilon_{coat}\) indicated in the figure).
Taking the values for the coating dielectric constant in the range $3 \leq \varepsilon_{\text{coat}} \leq 8$, then the ratio $\phi_{\text{BS}}/\phi_{\text{BK}}$ or $\phi_{\text{SE}}/\phi_{\text{BK}}$ shall always be below 1.0 in all the reasonable situations considered, meaning that this model decreases the water uptake estimate compared to the BK equation (Fig. 7).

Boettcher equation (5) can also be written using capacitance values instead of dielectric constant. In that form, it can also be compared with equation (22), giving:

$$\phi_{\text{BS}} = \phi_B \frac{3C}{2C + C_{\text{sol}}}$$

where $\phi_{\text{BS}}$ corresponds to the water absorption calculated by Eq. (22') and $\phi_B$ refers to the Boettcher equation. $C$ and $C_{\text{sol}}$ refer to the coating capacitance and the water capacitance, respectively, and $C_0$ symbolizes the capacitance extrapolated to $t = 0$. Since normally $C_{\text{sol}} \gg C$, then the new model can also be expected to give lower water fractions than the Boettcher equation.

From the above exposed, it can be concluded that the linear model now derived improves the estimates of water uptake based upon capacitance measurements, when compared to other models.

4. Conclusions

A model to estimate the water content in a polymeric coating based upon capacitance measurements was presented. The model describes the organic coating as a simple RC circuit, although this description is compatible with a random distribution of elements with different properties. The model improves the estimation of water content made by the Brasher–Kingsbury equation, decreasing the discrepancy with gravimetric results.

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Appendix A

The determination of the capacitance for each component (air, solution, coating) leads to difficulties in the choice of the area and thickness to use, especially for the solution and air.

Knowing that the isolated solution zones are scattered throughout the film, then the film can be described by a summation of layers of thickness $\delta d = d/H$, where $H$
represents the number of layers and $d$ is the total film thickness. For each layer there are disconnected solution areas represented by $A'_{sol}$, and the expression for the admittance of the solution in that layer can be stated as follows:

$$ Y_{sol} = \frac{j \omega \varepsilon_{sol} \varepsilon_0}{\delta d} (A'_{sol} + A'^2_{sol} + \cdots + A'^q_{sol} + \cdots) \iff Y_{sol} = \frac{j \omega \varepsilon_{sol} \varepsilon_0 A_{sol}}{\delta d} \quad (A.1) $$

It can thus be concluded that the solution areas at each layer, $A'_{sol}$, can be summed, from the electrical point of view, forming a virtual capacitance. The film can be obtained by the recombination of all the layers, and since they are configured in series, then the film impedance results from the summation of the impedance of the individual layers, giving:

$$ \sum_{i=1}^{H} Z_{sol,i}^{cond} = \frac{1}{j \omega \varepsilon_0} \sum_{i=1}^{H} \frac{\delta d}{e_{coat} A'_{coat} + e_{air} A'_{air} + e_{sol} A'_{sol}} \quad (A.2) $$

Considering that $A'_{p} = \bar{A}_{\rho} r_{i,\rho}$, in which $\bar{A}_{\rho}$ represents the average area for the $\rho$ component and $r_{i,\rho}$ a factor expressing the deviation from the average in each layer, then the resulting expression can be re-written as

$$ \sum_{i=1}^{H} Z_{sol,i}^{cond} = \frac{1}{j \omega \varepsilon_0} \sum_{i=1}^{H} \frac{\delta d}{e_{coat} \bar{A}_{coat} r_{i,coat} + e_{air} \bar{A}_{air} r_{i,air} + e_{sol} \bar{A}_{sol} r_{i,sol}} \quad (A.3) $$

If the concentration of water is approximately constant throughout the film (assumption c), then $r_{i,\rho} \approx 1$, resulting an equation identical to the expression (13), where each component capacitance properties can be considered as a virtual global capacitor with the expression of the capacitance given by

$$ Z = \frac{d}{j \omega \varepsilon_0 (e_{coat} \bar{A}_{coat} + e_{air} \bar{A}_{air} + e_{sol} \bar{A}_{sol})} \quad (A.4) $$

It must be said that the high frequency approximation, not used in the deduction, would lead to a similar result, since the impedance resulting from the ionic conduction must be constant in each layer, as a consequence of premise (c).

References