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EQUIVALENT CIRCUIT MODELS FOR AC IMPEDANCE DATA ANALYSIS

By M.D. Danford

Materials and Processes Laboratory
Science and Engineering Directorate

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16. Abstract

A least-squares fitting routine has been developed for the analysis of ac impedance data. It has been determined that the checking of the derived equations for a particular circuit with a commercially available electronics circuit program is essential. As a result of the investigation described in this report, three equivalent circuit models have been selected for use in the analysis of ac impedance data at this laboratory.

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INTRODUCTION

An electrochemical cell can be represented by a purely electronic model. For example, an electrode interface during an electrochemical reaction is analogous to an electronic circuit consisting of an array of resistors and capacitors. In this representation lies the utility of alternating current (ac) impedance techniques, since it allows the researcher to characterize the electrochemical system in terms of an "equivalent circuit."

Of particular relevance is a well-developed branch of ac theory concerned with the response of a given circuit to an ac or voltage as a function of frequency. For an ac, a voltage E (volts) can be applied to a circuit, the resulting current I (amps) measured, and the impedance Z (ohms) can be calculated, the equation being:

$$E = IZ \quad . \tag{1}$$

Here, the impedance Z is the ac equivalent of resistance. The vector expression for ac impedance is:

$$Z_{\mathrm{TOTAL}} = Z' + jZ'' \quad . \tag{2}$$

Here, Z' is the real part of the impedance vector, jZ'' is the imaginary part, and $j = \sqrt{-1}$.

The absolute magnitude of the impedance vector can be expressed as:

$$|Z| = [(Z')^2 + (Z'')^2]^{1/2} \quad , \tag{3}$$

and the phase θ is defined by:

$$\tan\theta = Z''/Z' \quad . \tag{4}$$

In the present work, much use is made of the Bode magnitude curve, obtained by plotting $\log |Z|$ versus $\log \omega$ ($\omega = 2\pi f$) and the Bode phase curve, obtained by plotting θ versus $\log \omega$. The observed Bode magnitude curve is fitted by a nonlinear least-squares program ORGLS [1] to that calculated using an appropriate equivalent circuit model, with each of the resistor and capacitor components in the circuit being a variable parameter. After fitting the Bode magnitude curve, the Bode phase curve is calculated using the parameters obtained from the least-squares fit.

It is the purpose of this report to present the results of an investigation of several possible equivalent circuit models, a necessary step in the selection of a model or models which adequately account for the response of a corroding system to an applied ac voltage. It is necessary to derive equations which describe the response of particular electronic circuits and to enter them appropriately into a user's subroutine for calculating both the values of the impedance $|Z|$ and derivatives for manipulation in the least-squares procedure. A detailed mathematical description of that procedure is beyond the scope of this report. It is imperative that the accuracy of equation derivations and their entry into the least-squares program be carefully checked. Improper derivation, parameter number, or sign can destroy the validity of the results. In the present case, a commercial electronic circuit program, MICROCAP II [2], was employed, and phases calculated by the least-squares equations were compared with those calculated with MICROCAP II. In all cases where pure resistors and capacitors were employed in the circuit, agreement was exact. In models where the Warburg impedance, or impedance due to diffusion polarization existed, its effect was approximated by a resistor and capacitor in series in MICROCAP II. In these cases, agreement was not exact, but was sufficiently close to verify the correctness of the equation set up in the least-squares program.

DISCUSSION

A list of symbol definitions used in the various models is given in table 1. Equivalent circuit model RC2, the model of Kendig, et al. [3], is shown in figure 1 along with observed and calculated curves for the Bode phase and Bode magnitude. Each of the models to be discussed was fitted separately with the least-squares routine using the parameters appropriate for each. The fit of the Bode magnitude curve is quite good, but deficiencies occur in the Bode phase fit which is more sensitive. The fit of the Bode phase curve is poor at both low and high frequencies. The calculated phase tends toward zero at high frequency, whereas the observed curve remains high and undoubtedly would increase if the frequency range were extended.

The model of Sluyters [4], model RC3, is shown in figure 2. This model includes, for the first time, the effect of diffusion polarization or the Warburg impedance. As the observed and calculated curves show, the fits of the observed and calculated curves is very poor for both the Bode phase and Bode magnitude.

Model RC4 is shown in figure 3. This model, in addition to the parameters of model RC3, includes an overall coating capacitance C_C and pore resistance R_P. As the observed and calculated curves show, agreement is much better in this case, and the fits are comparable to those for model RC2.

Model RC5 (fig. 4, top), similar to model RC3 except that a capacitor representing the effect of a chemical reaction is included, failed to converge on least-squares refinement. Another model, model RC6 (fig. 4, bottom) which included a charge transfer capacitance C_{DL} in parallel with a segment having a Warburg impedance and also in parallel with a third segment having a second Warburg impedance in series with a pore resistance R_p, also failed to converge in the least-squares procedure. Too many circuit paths are available so that an increase of impedance along one path and a decrease in another path compensate each other. As a result, a great deal of parameter interaction occurs and results in failure of the model.

Model RC7 is shown in figure 5. This is the model proposed by Cahan and Chen [5] in connection with a study on the kinetics of O_2 evolution on oxide-covered metals. This model begins to take into account the contributions of the coating-electrolyte contribution to the impedance. The fits of the observed and calculated curves are quite good, comparable to those for model RC2. Discrepancies in the phase fits again are apparent at both low and high frequency. The calculated phase again tends toward zero at high frequency. That parameters from the coating-solution interface are important is evidenced by the precision of their determination in the least-squares procedure. Model RC8 (fig. 6), which includes a Warburg impedance rather than the charge transfer arrangement of model RC7, exhibits fits of about the same quality.

Model RC9 which, in addition to the parameters of model RC7, contains an overall solution capacitance C_S, is shown in figure 7. The observed and calculated curves for the Bode magnitude fit are in excellent agreement. The calculated Bode phase curve again shows discrepancies at low frequency, but starts to rise at high frequency, in better agreement with the observed curve. The Bode phase curves for models RC2 and RC9, calculated with MICROCAP II and extending to higher frequency, are shown in figures 8 and 9. As shown by these figures, the curve for model RC9 continues to rise at higher frequency, while that for model RC2 tends further toward zero. Further evidence for the increased effectiveness of model RC9 is shown in figure 10 for the case of primer-coated 2219-T87 aluminum [6]. Here both the observed and calculated phase curves rise at high frequency, while the curve for model RC7 obviously goes to zero. Thus, better agreement is obtained at high frequency for model RC9. This model has proven to be almost universally applicable to coated metal surfaces, even for primer-topcoat combinations [7].

Model RCX is shown in figure 11. This model, in addition to the parameters of model RC9, contains a parameter C_{CR} which represents the contribution of a chemical reaction due to the corrosion process. As shown by the observed and calculated phase curves, agreement is finally achieved at low frequency, while the quality of fit at higher frequency remains about the same as that for model RC9. A drawback is that good low frequency data (beginning at 0.001 Hz and extending to about 1 Hz) are sometimes difficult to obtain. As a result, a least-squares fit of the Bode magnitude data is impossible. The fact that the parameter C_{CR} is due to a chemical reaction is attested to by the linear relation between values of C_{CR} and the corrosion currents obtained with the polarization resistance technique [7]. Model RC13 (fig. 12), which contains the Warburg impedance parameter rather than the charge transfer parameters of model RC9, also exhibits fits of good quality, comparable to those for model RC9. In this case also, a least-squares fit of the data is sometimes impossible. The least-squares fit of model RC9 is almost always successful, with all parameters being well determined, and that circuit has been selected as the prime model for ac impedance work at this laboratory. Models RCX and RC13 are also used where possible.

CONCLUSION

It is necessary to verify the correctness of the derived equations for equivalent circuits representing the response of coated samples to an alternating current or voltage. This can be accomplished with commercially available electronic circuit programs.

As a result of this investigation, three models have been selected as providing the best representation of the response of a corroding system to ac voltages or currents. These models seem to be universally applicable to all types of coated surfaces and are fitted in excellent fashion to the observed Bode magnitude curves by the method of least squares.

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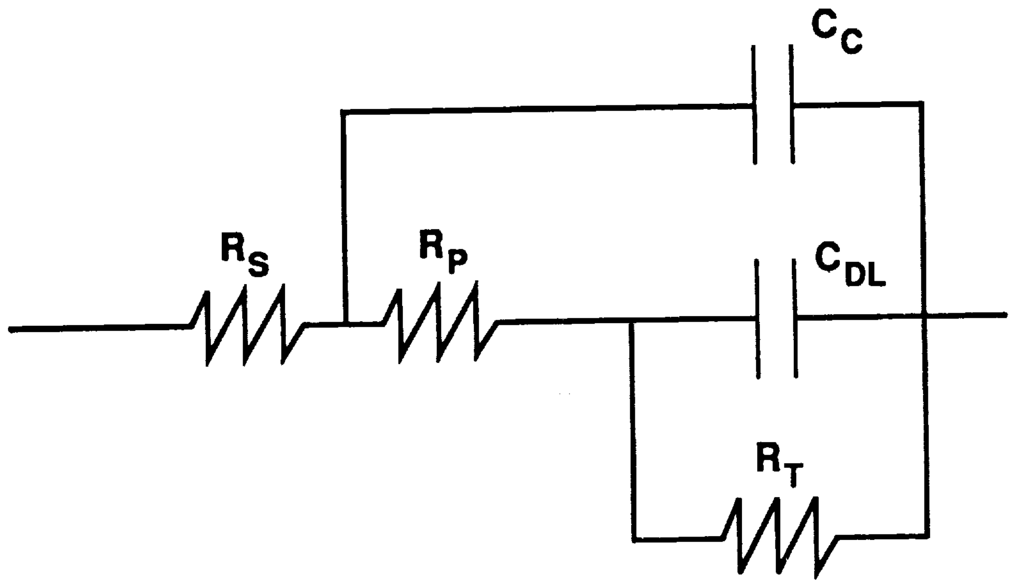
Table 1. Parameter definitions for the ac impedance equivalent circuit models.

C_S	Solution Capacitance
R_S	Solution Resistance
C_F	Faradaic Capacitance
R_F	Faradaic Resistance
C_C	Coating Capacitance
R_P	Pore Resistance
R_{CR}	Chemical Reaction Resistance
C_{DL}	Metal/Coating Interface Capacitance
R_T	Charge Transfer Resistance
C_{CR}	Chemical Reaction Capacitance
Z_W	Warburg Impedance (Diffusion Polarization)



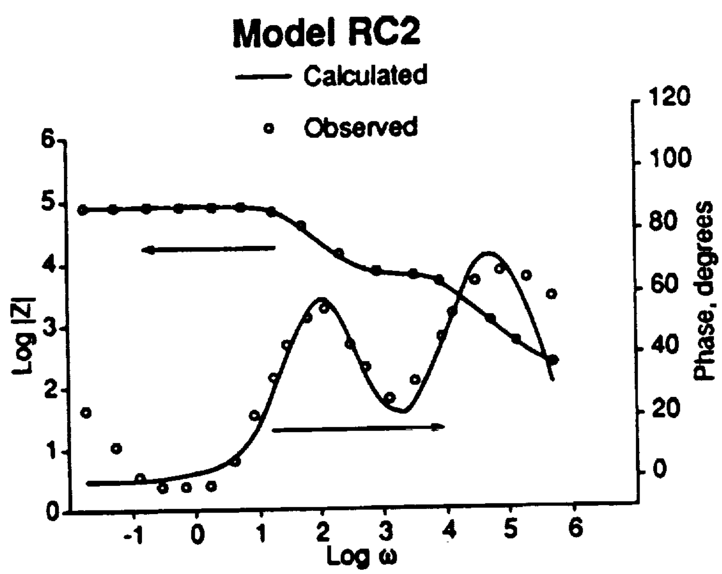


Figure 1. Equivalent circuit, observed and calculated curves for model RC2.

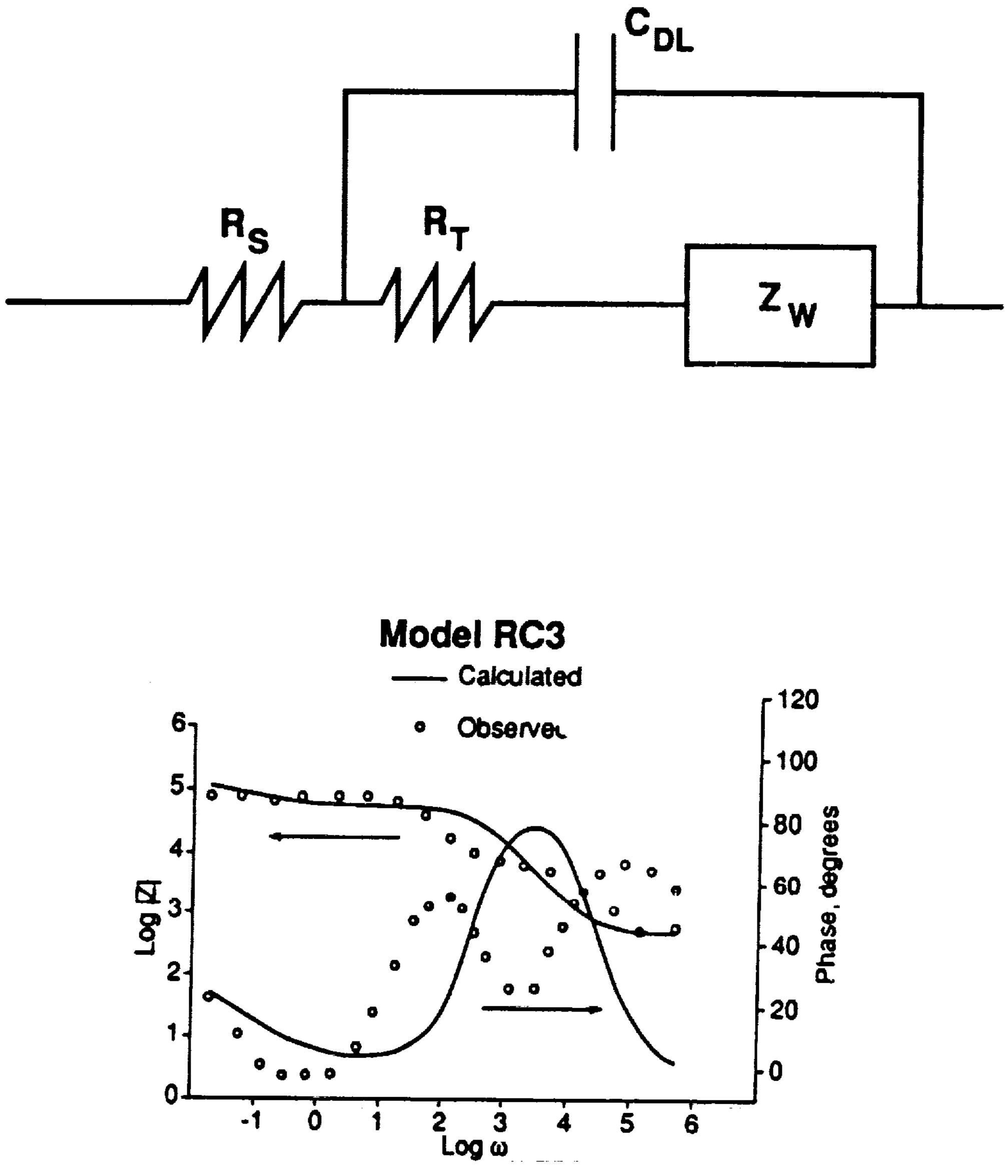


Figure 2. Equivalent circuit, observed and calculated curves for model RC3.

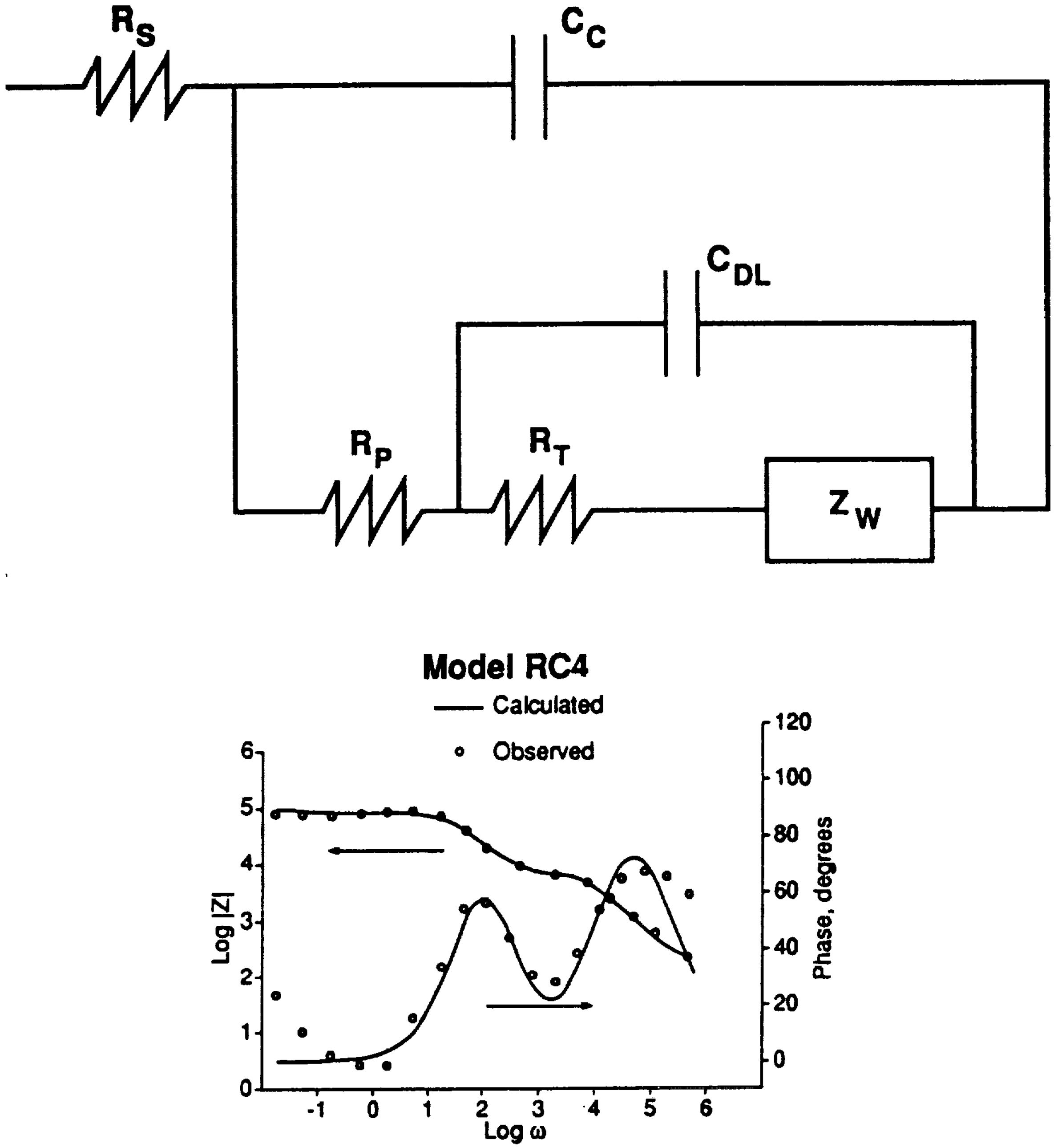
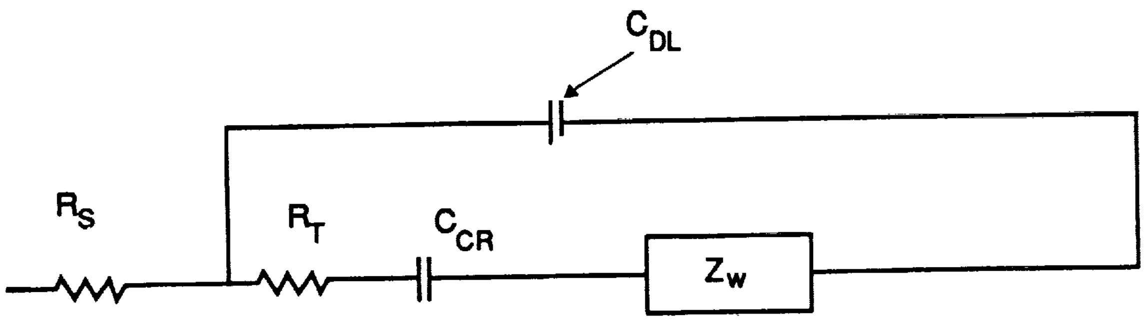
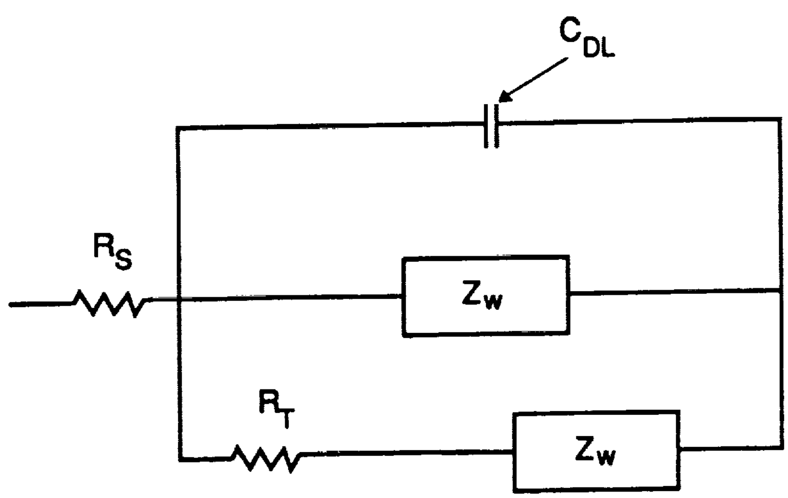


Figure 3. Equivalent circuit, observed and calculated curves for model RC4.



RC5



RC6

Figure 4. Equivalent circuit models RC5 and RC6.

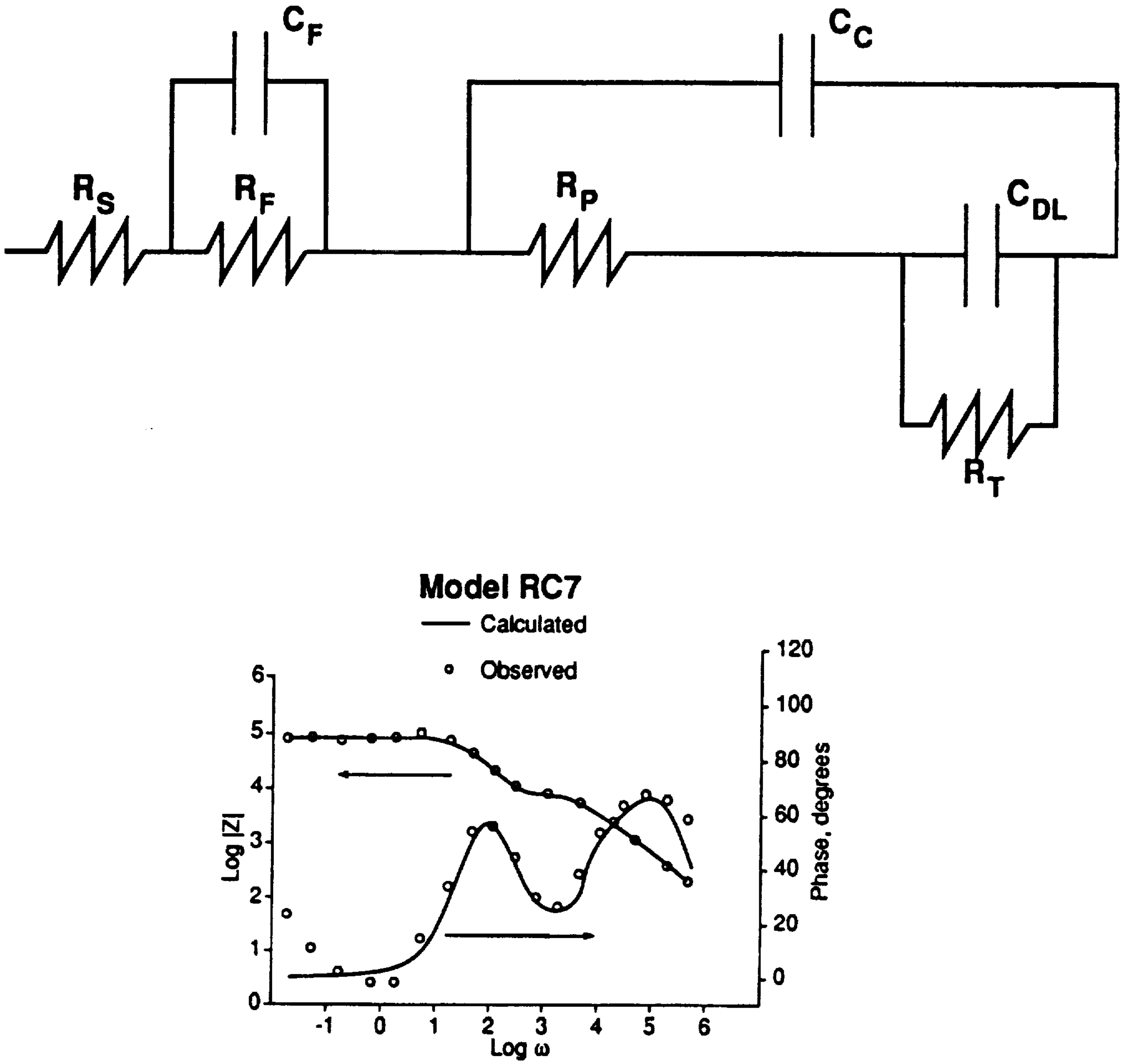


Figure 5. Equivalent circuit, observed and calculated curves for model RC7.

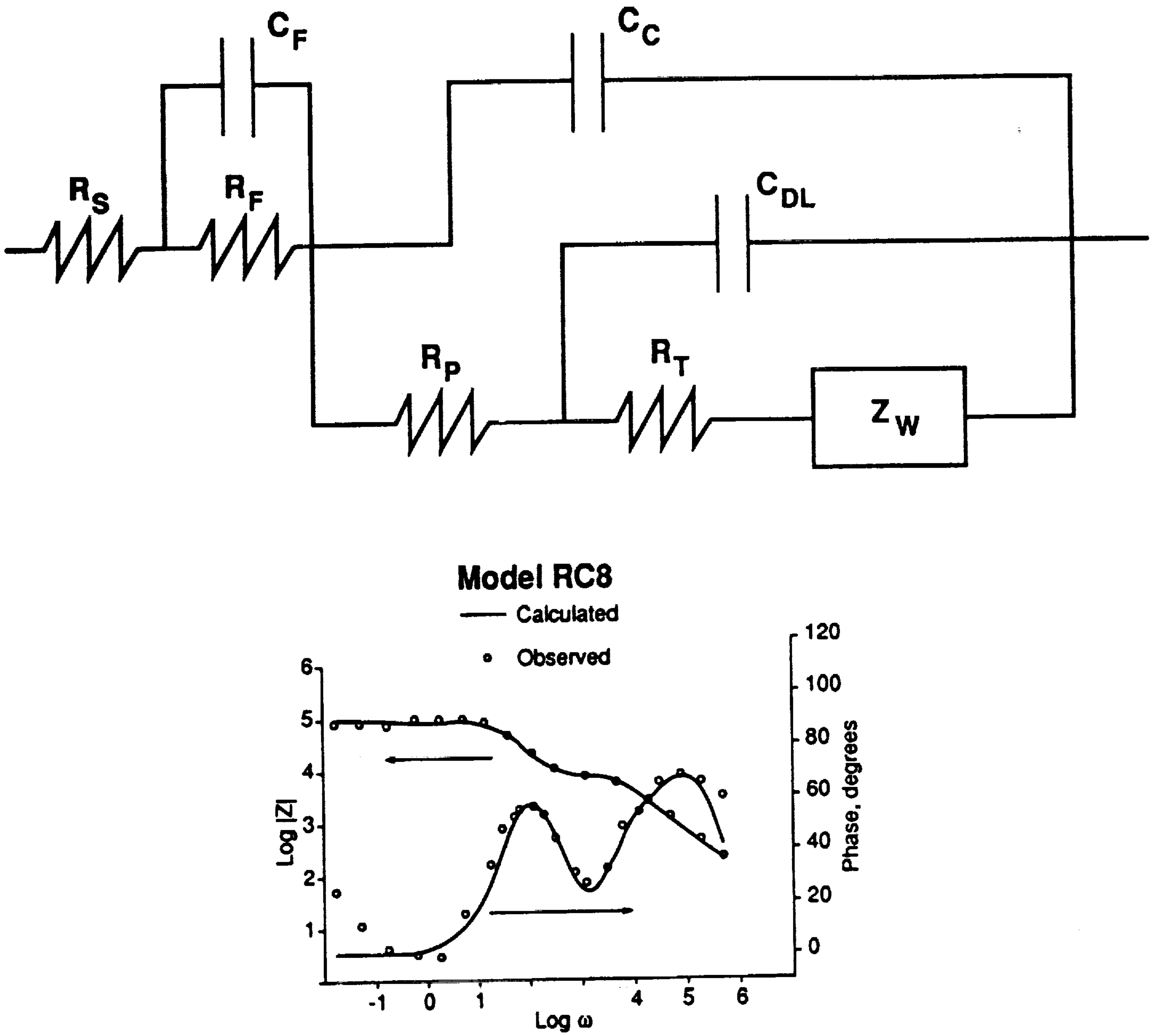


Figure 6. Equivalent circuit, observed and calculated curves for model RC8.

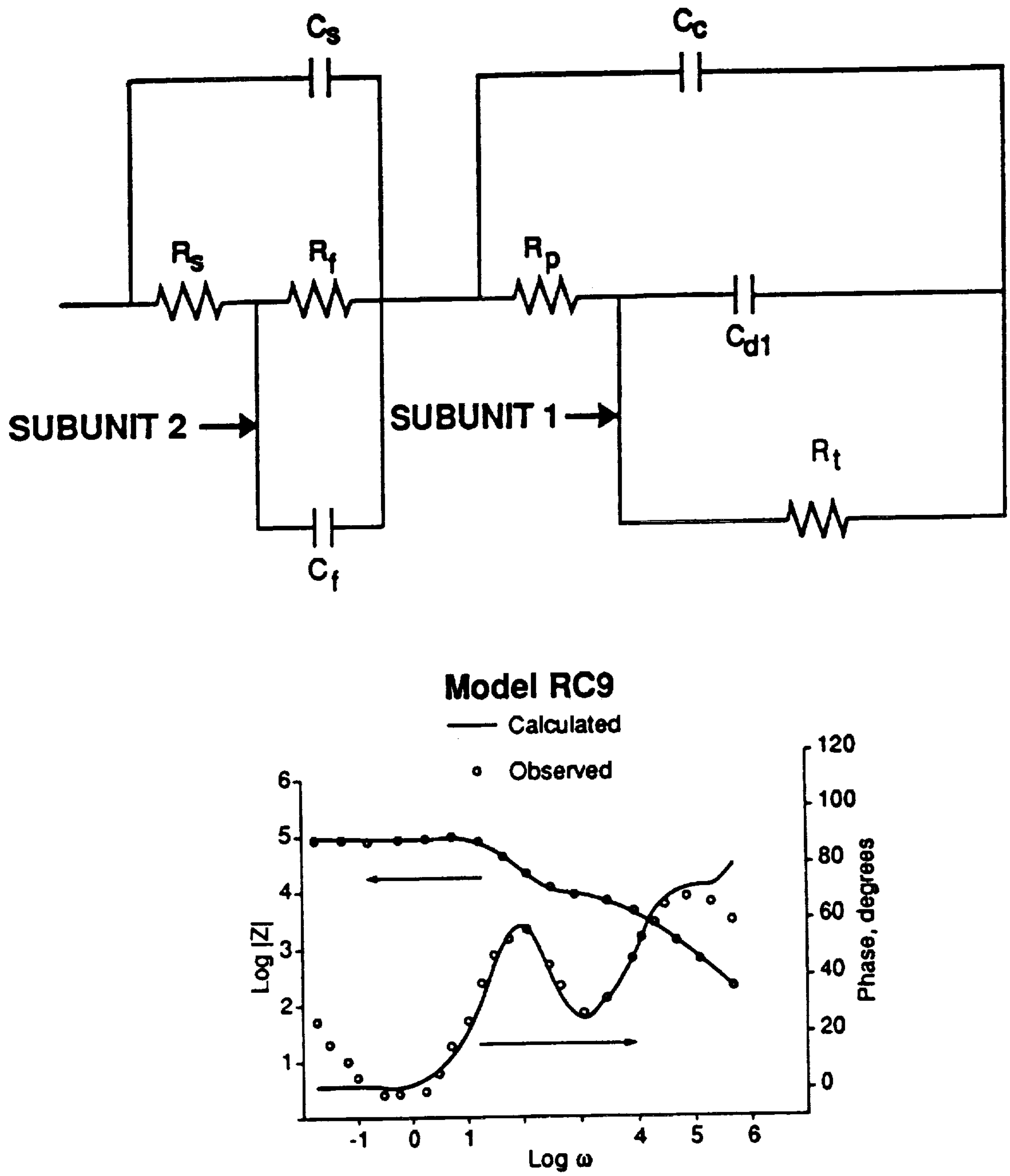


Figure 7. Equivalent circuit, observed and calculated curves for model RC9.

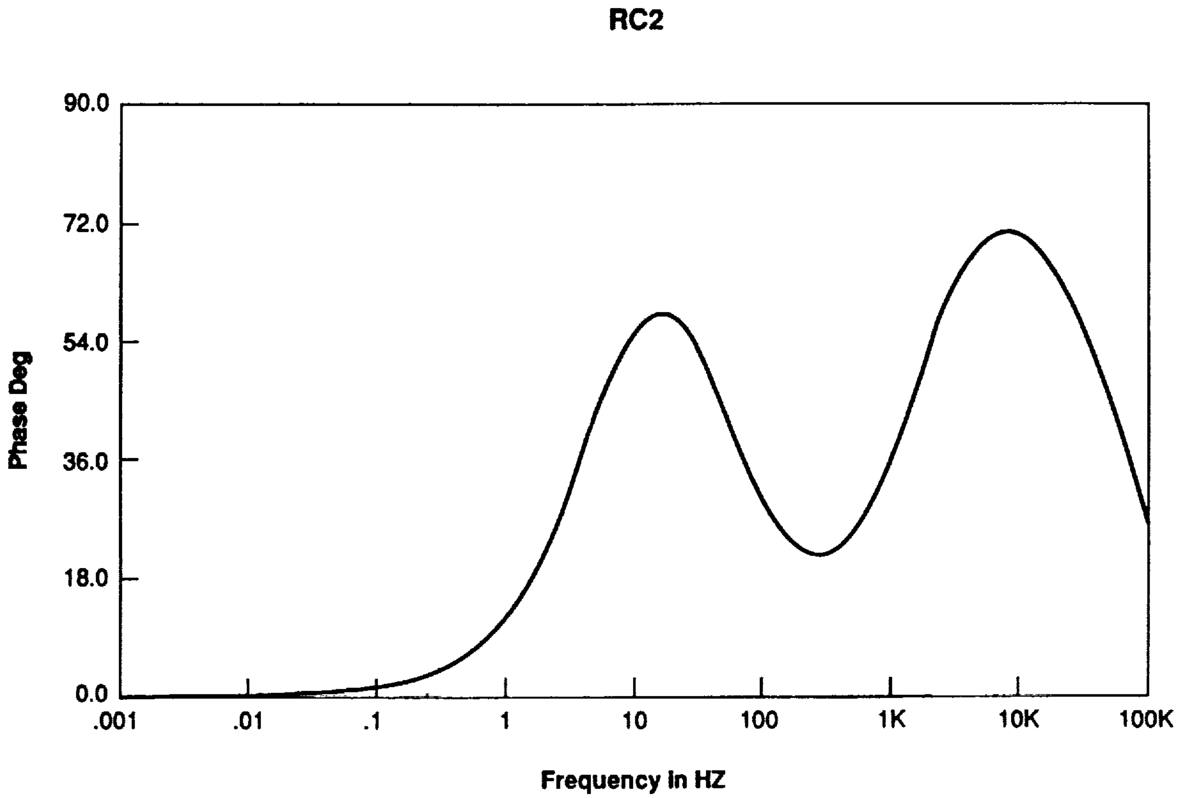


Figure 8. Bode phase for model RC2 calculated with MICROCAP II.

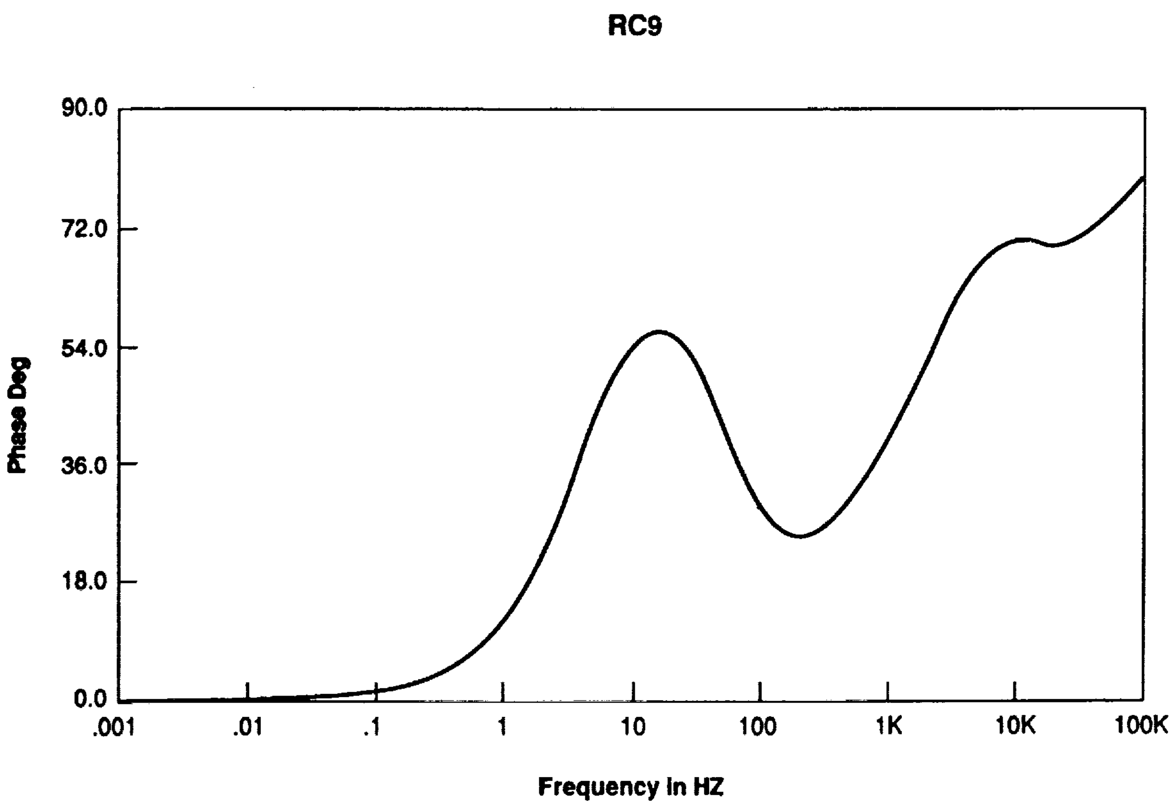


Figure 9. Bode phase for model RC9 calculated with MICROCAP II.

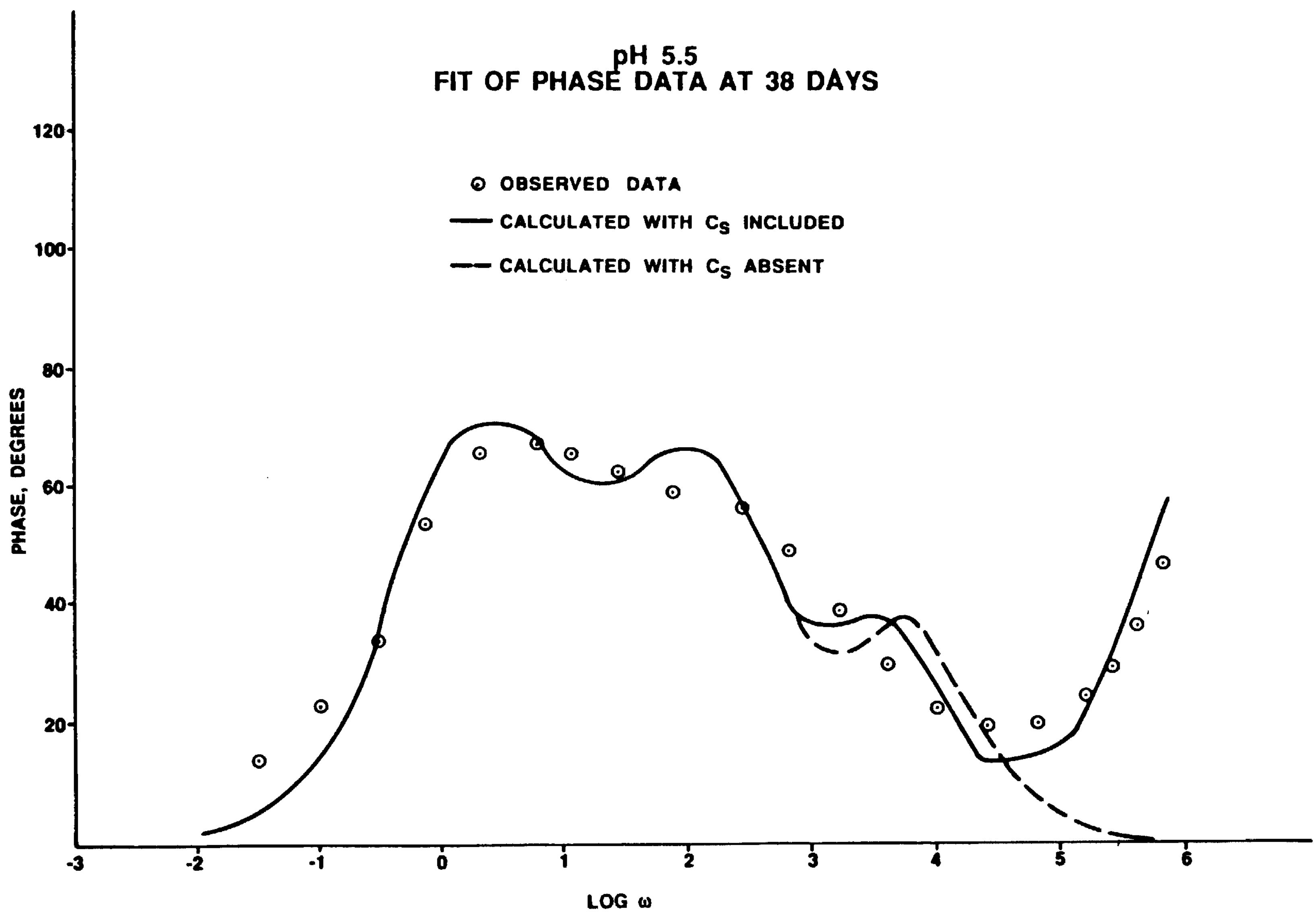


Figure 10. Bode phase curves calculated for models RC7 and RC9 with observed curve for coated 2219-T87 aluminum.

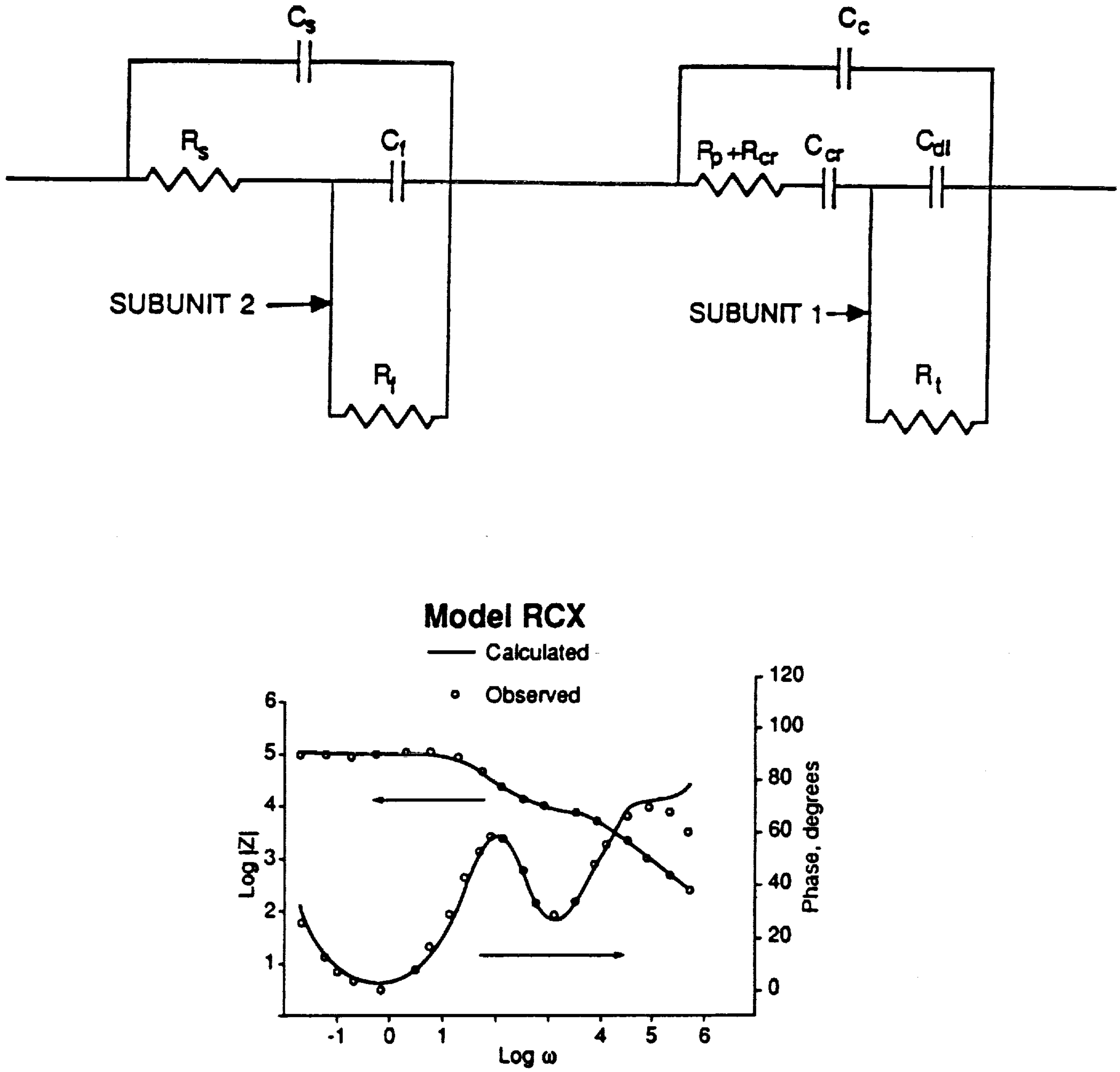
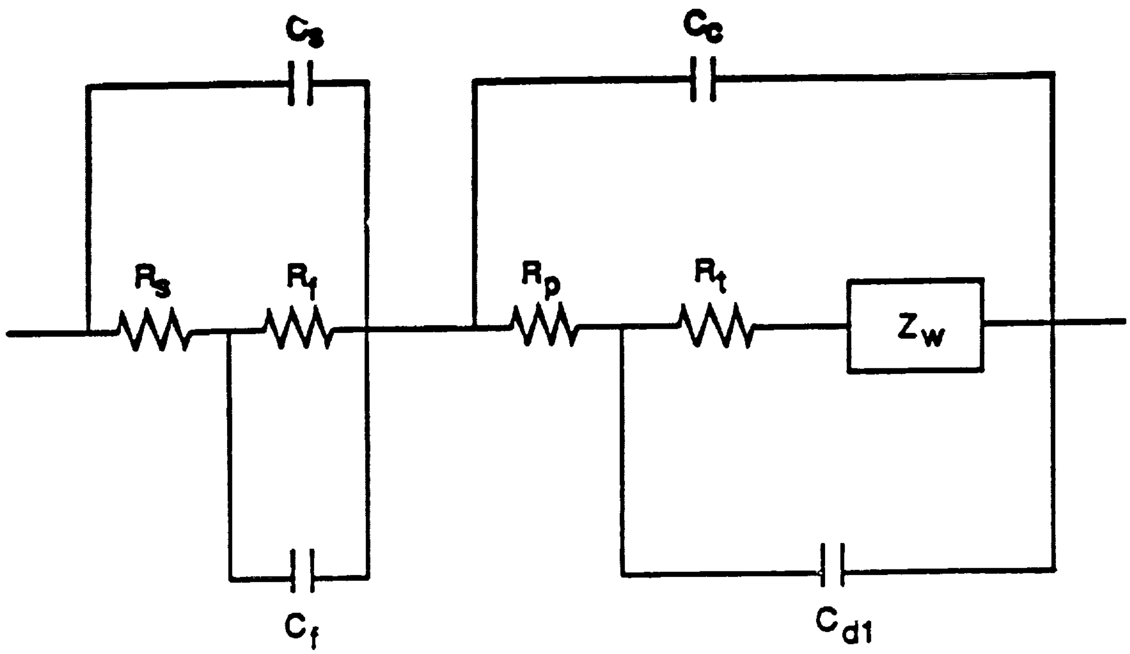


Figure 11. Equivalent circuit, observed and calculated curves for model RCX.



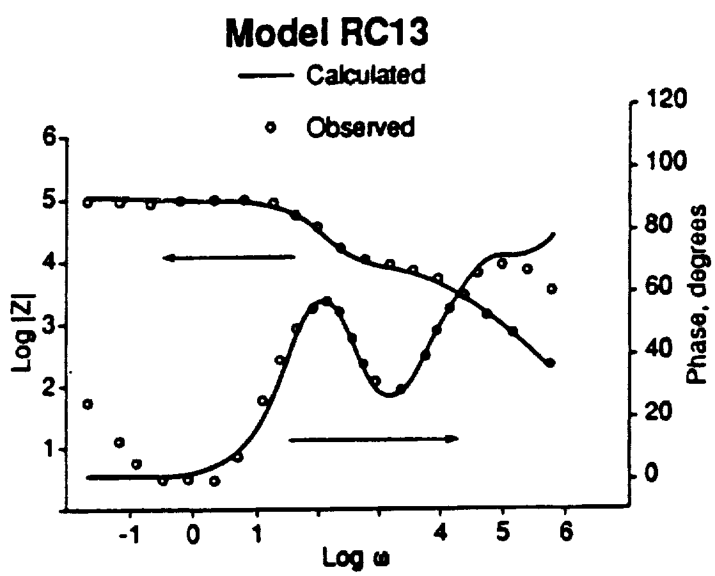


Figure 12. Equivalent circuit, observed and calculated curves for model RC13.

APPROVAL

EQUIVALENT CIRCUIT MODELS FOR AC IMPEDANCE DATA ANALYSIS

By Merlin D. Danford

The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

J. W. Montano

J. W. MONTANO
Chief
Corrosion Research Branch

Paul M. Munafo

PAUL M. MUNAFO
Chief
Metallic Materials Division

Paul H. Schuerer

PAUL H. SCHUERER
Director
Materials & Processes Laboratory

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