Prediction of Water Percolation Threshold of a Microemulsion Using Electrical Conductivity Measurements and Design of Experiments

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ABSTRACT: This paper presents the estimation of water percolation threshold (ϕc) of a nonionic microemulsion by studying its conductivity (σ) as a function of water volume fraction (ϕ). The initial solution of alkyl polyglycosides/glyceryl monooleate/n-octane/isopropyl alcohol with weight ratios of 3/3/2/2 was diluted by brine (1 wt % sodium chloride), and the electrical conductance was measured along the specific dilution line. One factor design (OFD), which is an approach embedded in Design of Experiments (DOE), was used to model the variation of d(logσ)/dϕ with ϕ. A quadratic equation with natural logarithm transformation was then fitted and validated. The model was optimized to predict ϕc, the water volume fraction at which d(logσ)/dϕ is a maximum. The predicted value of ϕc from the optimization of the model is 0.1245. In addition, fitting to the scaling law was conducted, and the value of ϕc, from this theoretical model was 0.1212. Apparently, these values are in excellent agreement. It is concluded that DOE can be used to estimate the value of ϕc for a microemulsion relatively precisely with less computation and restriction compared to the conventional fitting approach.

1. INTRODUCTION

Mixing different ratios of oil, water, a surfactant(s), and a cosurfactant(s) oftentimes yields different types of microemulsions, which are transparent, thermodynamically stable, macroscopically monophasic, and microscopically heterogeneous systems. On the basis of the ratio of the components, three different microstructures for a microemulsion system may be formed. At high oil content, water-in-oil (w/o) microemulsion appears consisting of water droplets dispersed in a continuous oil phase. At high water content, oil-in-water (o/w) microemulsion is formed consisting of oil droplets dispersed in a continuous water phase. At intermediate ratio of oil and water, a bicontinuous phase exists. The microstructure of a microemulsion can be altered from w/o to a bicontinuous system and from bicontinuous to an o/w system by increasing the water content at constant temperature or by increasing the temperature at constant water content. The structural transition in microemulsions has been elucidated by various techniques such as nuclear magnetic resonance (NMR), dynamic light scattering (DLS), dielectric relaxation, small angle neutron scattering (SANS), transmission electron microscopy (TEM), time-resolved fluorescence quenching (TRFQ), ultrasound, viscosity, and electrical conductance.1−5

Among these techniques, the application of electrical conductivity measurements has been very popular since useful information on micellar interaction could be obtained.5−8 Water percolation threshold is an important physical property of a microemulsion, which is frequently determined using electrical conductivity measurements.8−10 Water percolation threshold is an indicator of microstructural transition from w/o to bicontinuous microemulsion. Since the dispersed water droplets are clustering and changing to the continuous phase at water percolation threshold, a sharp increase in electrical conductivity (σ) is usually observed as a function of water content (ϕ) or temperature (θ).7,10−14 The abrupt rise in electrical conductivity at water percolation threshold occurs due to the change of the conductance medium. Below the water percolation threshold, the conductance medium is the continuous oil phase that contributes very little to the conductance. However, at the water percolation threshold, the dispersed water phase percolates and tends to form a continuous water phase. Therefore, at the water percolation threshold, the conductance medium of a very nonconductive oil continuous phase is changed to the highly conductive water phase. Consequently, its electrical conductivity increases tremendously.

A similar percolation process has been studied extensively for w/o microemulsions with either ionic or nonionic surfactants.10−13,15,16 Theoretical models such as the effective medium theory and scaling law models have been utilized to analyze the conductivity results.10,12,13,15,17−20 The water percolation thresholds (ϕc, θc) of these reverse microemulsions have been obtained by numerical analysis of the models with adjustment by the least-squares method.10,12,13,15,17−20 ϕc is the water-induced water percolation threshold that occurs when the water content (ϕ) increases at constant temperature. Meanwhile, θc is the temperature-induced water percolation threshold, which occurs when the temperature (θ) increases at constant water content.

It has been reported that the percolation threshold value can also be estimated numerically from the maximum of d(logσ)/dϕ.
\( d\phi \) versus \( \phi \), and the estimated value from this methodology is relatively close to the final predicted value from the fitting methodology.\(^{8,21-23}\) The application of the first methodology in the estimation of percolation threshold was found to be very ambiguous and complicated. This is because the theoretical models, which were fitted in the first methodology, are only valid close to the percolation threshold and they are not applicable to infinite dilution and immediate vicinity of the percolation threshold.\(^{8,22,23}\) Therefore, there are many restrictions in its application. On the other hand, the application of the first methodology to estimate percolation threshold requires tremendous numerical calculations. Different equations have been obtained theoretically at below and above percolation threshold, and these equations have to be fitted simultaneously to the experimental electrical conductivity data.\(^{8,22,23}\) Thus, the second methodology of percolation threshold estimation was superior to the first methodology. Without the knowledge of the percolation theoretical models, the percolation threshold can be predicted from numerical optimization of \( d(\log r)/d\phi \) against \( \phi \), by finding the water content at which \( d(\log r)/d\phi \) has the maximum.\(^{8,21-23}\)

Compared to the traditional numerical optimization, which requires many experimental data to ensure high prediction accuracy, Design of Experiments (DOE) is one of the systematic approaches in problem solving which is applicable to data collection and statistical analysis. The primary objective of designing an experiment statistically is to ensure that valid results are obtained with minimum effort, time, and resources.\(^{24-26}\) Statistical experimental design has recently been applied on microemulsion.\(^{27}\) However, it has seldom been used to optimize the value of \( d(\log r)/d\phi \) to find \( \phi_c \) of a microemulsion. In this work, the application of DOE in this specific area was conducted by comparing the predicted value of \( \phi_c \) obtained from DOE to the estimated value of \( \phi_c \) from fitting methodology using electrical conductance experimental data on a specific dilution line. Design Expert software was used to run response surface methodology (RSM) and perform one factor design (OFD). MATLAB software was used for simultaneous curve fittings for both equations, below and above percolation, to the experimental electrical conductivity data.

2. MATERIALS AND METHODOLOGY

2.1. Materials. The surfactant used in the formulation of the microemulsion in this study was Glucopon 650EC, which is a mixture of alkyl polyglycosides (APG) having an average alkyl chain length of 11, Hydrophilic–Lipophilic Balance (HLB) of 11.9, and Critical Micelle Concentration (CMC) of 0.073 g/L at 37 °C.\(^{28}\) It was supplied by Cognis (Malaysia) Sdn. Bhd. which is part of BASF Chemical Company. In addition, sodium chloride (NaCl, A.R. grade) and isopropanol alcohol (IPA, A.R. grade) used in the microemulsion were supplied by LGC Scientific, Malaysia. Finally, n-octane (free of olefins) and glycerol monooleate (GM) were supplied by Sigma-Aldrich Sdn. Bhd., Malaysia.

2.2. Pseudoternary Phase Diagram and Microemulsion Preparation. The phase behavior of a system consisting of brine, oleic, and surfactant solutions is described on a pseudoternary phase triangle instead of a multidimensional phase diagram for convenience. It is evident that fixed weight ratios must be selected for the surfactant and oleic solutions and two of the triangle vertices represent 100% of these binary mixtures. The nonionic surfactant solution used in this study was a blend of APG and GM at mixing ratio (w/w) of unity. The oleic solution consists of n-octane and IPA as cosurfactant with mixing ratio (w/w) of unity. The aqueous solution was brine with salinity of one weight percent (wt %) NaCl. The water used in the brine preparation was deionized water with electrical resistivity of 18.2 MΩ·cm (Sartorius, arium 611UF ultrapure water system). In order to construct the phase diagram for the system, ten samples at different ratios of surfactant and oleic solutions were prepared. All the prepared samples were titrated with the brine under constant stirring condition at 25 ± 0.5 °C until they became cloudy. The composition of each sample at the moment of clouding was recorded. The measurements were checked several times for reproducibility, and the compositions were expressed in wt %. All the ten composition data were shown on a ternary diagram to produce a boundary demarcating the one phase (1\(\phi\)) and two phase (2\(\phi\)) regions. The 1\(\phi\) region demonstrates the system composition range at which a clear w/o microemulsion can appear.

2.3. Electrical Conductivity Measurements. The initial solution consists of 40 wt % oleic and 60 wt % surfactant solutions. The initial solution was diluted with brine, drop by drop, and thoroughly mixed. The electrical conductivity of the w/o microemulsion was measured in each step at constant temperature of 25 ± 0.5 °C along the N60 dilution line, which passes through the 1\(\phi\) region. The conductivity meter used was Metrohm, 712 Conductometer. The electrode material was platinum, and the cell constant was 0.845 cm\(^{-1}\) ± 1%. The conductometer can be used to make measurement between 0 \(\mu S/cm\) and 2000 mS/cm. Since the surfactant solution was nonionic, brine with high salinity of 1 wt % NaCl (about 0.167 M sodium chloride) was used in the dilution of the solutions so that the electrical conductance could be detected. The electrode was dipped in the microemulsion sample while the sample reached equilibrium, and the value of the electrical conductivity was recorded when the reading was stable. Experiments were conducted in triplicate, and the average of the experimental data was used in the next steps. The cell constant was calibrated using standard KCl solutions and checked several times.

2.4. Estimation of Water Percolation Threshold by Fitting the Theoretical Model. This paper applies the most widely used theoretical model for the conductivity of w/o microemulsion which is valid close to the percolation threshold at constant temperature.\(^{8,22,23}\) This theoretical model, which is based on the study of dynamic interdroplet interactions at percolation, is called the scaling law.\(^{14,17}\) It is given as follows:

\[
\sigma = \begin{cases} 
A(\phi_c - \phi)^s & \text{if } \phi < \phi_c \\
B(\phi - \phi_c)^s & \text{if } \phi > \phi_c
\end{cases}
\]

Equations 1 and 2 are only valid below and above the percolation threshold, respectively. The value of exponent \( s \) is usually taken between 1.5 and 2, while the value of the exponent \( t \) can be lower or higher than 1 based on the percolation regime. When the calculated value of exponent \( s \) is less than 1, the percolation regime is called static. It corresponds to the appearance of bicontinuous microemulsions. On the other hand, when the calculated value of exponent \( s \) is higher than 1, the percolation regime is classified as dynamic. It corresponds to the appearance of water channels during the rapid processes of fusion and fission among the droplets.
The above two equations were fitted simultaneously to the experimental electrical conductivity data. The numerical coefficients $A$ and $B$, and the critical exponents, $s$ and $t$, as well as the percolation threshold ($\phi_c$) were determined by numerical analysis thru adjustment by the least-squares method. Curve fitting toolbox of MATLAB software was used in the fitting process.

2.5. Prediction of Water Percolation Threshold by Optimization Using DOE. RSM is a common and promising statistical method of DOE which provides the regression model equation(s) and operating conditions using the data from appropriate and certain experiments. Thus, RSM has been applied to statistically determine an approximating function in predicting future responses and optimizing the response function. One factor design (OFD), which is a simple RSM design, was used in this study to model the trend of $d(\log \sigma)/d\phi$ with $\phi$ and optimize the model to find $\phi_c$. It was assumed that the water content ($\phi$) is the only factor that affects the response, $d(\log \sigma)/d\phi$, at constant temperature. Thus, OFD is a suitable technique of RSM in this specific modeling case. Design Expert software version 8.0.7 (STAT-EASE Inc., Minneapolis, USA) was used to carry out OFD. In OFD, a quadratic model was developed to predict the single-response as a function of the single-variable. The coefficients of the model were determined using the regression analysis technique in the OFD. Analysis of variance (ANOVA) was used to justify the adequacy of the model. The final model was maximized to estimate the water content at which $d(\log \sigma)/d\phi$ is at a maximum. The predicted water content corresponds to the water percolation threshold ($\phi_c$).

3. RESULTS AND DISCUSSION

3.1. Pseudoternary Phase Diagram. Figure 1 presents the pseudoternary phase behavior of the system brine/APG/GM/n-octane/IPA at 25 ± 0.5 °C. The mixing ratio (w/w) of APG/GM equals unity. In addition, the mixing ratio (w/w) of n-octane/IPA equals unity. The one and two phase regions are designated by 1$\phi$ and 2$\phi$, respectively. The green boundary demarcating the two regions was plotted using the ten composition data at which cloudiness was observed. The red line in Figure 1 is the water dilution line, N60, where the weight ratios of APG/GM/n-octane/IPA are equal to 3/3/2/2. It is obvious that the percolation conductance has been studied at the compositions along the dilution line, which always lies in the 1$\phi$ region, and therefore, the percolation process is not disturbed by the complexity of multiphase formation.

3.2. Electrical Conductivity Measurements. Figure 2 shows the measured electrical conductivity of the w/o microemulsions at various water contents. The range of the
water content at which the electrical conductivities of the microemulsions were measured was selected on the basis of the applicability and efficiency of the test. The minimum value of water content in Figure 2 cannot be selected as zero because, in the absence of brine, the nonionic initial solution has almost zero electrical conductivity. The maximum value of water content in Figure 2 was selected at about 0.2 water content because water percolation threshold has already taken place within this range of water content.

Figure 2 shows that the microemulsions are relatively resistant to electrical conductance up to a specific water content value. At this point, the microemulsion tends to be more conductive with the increase of water content. These experimental data were used later in this work to predict the water percolation threshold by two different methodologies.

3.3. Numerical Fitting to the Scaling Law. Simultaneous numerical analysis of eqs 1 and 2 was conducted with adjustment to the experimental electrical conductivity data by the least-squares method using MATLAB curve fitting toolbox. Computation shows that the percolation threshold ($\phi_c$) occurs at 0.1212 water content. Furthermore, $A$, $B$, $s$, and $t$ are found to be 0.9634, 325070, 0.651, and 1.7, respectively. As expected, the exponent $t$ was found to be in the range of 1.5 to 2. Since the calculated value of exponent $s$ is less than 1.0, the percolation regime is classified as static. In the other words, bicontinuous microemulsion systems seem to appear above the percolation threshold. In Figures 3 and 4, the fittings to the scaling law are compared to the best possible polynomial fitting of the electrical conductivity data below and above the percolation threshold, respectively. Tables 1 and 2 show the coefficients of the fitted models and the goodness of the fit for fittings in Figures 3 and 4, respectively. According to these tables, scaling law seems to be fitted successfully for both data below and above the percolation threshold. This is because the $R$-squared and adjusted $R$-squared values are very close to 1.0 and the SSEs and RMSEs are relatively small. In addition, the quadratic polynomial model is relatively in good agreement with the experimental data above the percolation threshold.

3.4. Development of Regression Model Using DOE. The experimental values of electrical conductivity shown in Figure 2 were used in the plot of log$\sigma$ versus $\phi$. The slope of the curve was determined at specific water contents using MATLAB software. The value of $d$(log$\sigma$)/$d\phi$ against $\phi$ is
shown in Figure 5. As described previously, the water content at which $d(\log \sigma)/d\phi$ reaches its maximum value is defined as the water percolation threshold ($\phi_c$). Therefore, it is desirable to model $d(\log \sigma)/d\phi$ as a function of $\phi$ using DOE and optimize the model to predict $\phi_c$.

3.4.1. OFD Modeling. Considering that water volume fraction is the only factor which may influence $d(\log \sigma)/d\phi$, it was selected as the only factor of the modeling of the sole response of $d(\log \sigma)/d\phi$. Table 3 presents the design summary of the OFD modeling.

![Figure 5](image.png)

**Figure 5.** $d(\log \sigma)/d\phi$ as a function of water content.

The low and high values of water volume fraction were set on the basis of the minimum and maximum values of the experimental data in Figure 2. On the basis of the information in Table 3, the software automatically suggested seven experimental conditions to be performed. Then, the user conducted the tests at the determined conditions proposed by the model. The conditions of the seven experimental runs determined by the model and the corresponding experimental response values are presented in Table 4.

The quadratic model was selected as suggested by the Design Expert software. Regression analysis was performed to fit the response function of $d(\log \sigma)/d\phi$. The empirical model in terms of actual factors can be expressed as follows:

$$
\frac{d(\log \sigma)}{d\phi} = +50.80868 - 3396.11856\phi \\
+ 65075.52804\phi^2 - 4.27908 \times 10^5\phi^3 \\
+ 9.10638 \times 10^5\phi^4
$$

(3)

![Table 3](image.png)

**Table 3.** Design Summary

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<th>factor name</th>
<th>type</th>
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<th>high actual</th>
<th>low coded</th>
<th>high coded</th>
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<td>0.2018</td>
<td>-1.000</td>
<td>1.000</td>
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</table>

<table>
<thead>
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<th>ratio</th>
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<tbody>
<tr>
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<td>polynomial</td>
<td>2.6991</td>
<td>28.8908</td>
<td>10.7039</td>
</tr>
</tbody>
</table>

"Study type: response surface; design type: one factor; design model: quadratic; runs: 7.

The multiple regression analysis technique included in the OFD was used in the estimation of the model response coefficients.

Figure 6 shows the predicted $d(\log \sigma)/d\phi$ (derived from the model) versus actual $d(\log \sigma)/d\phi$ (obtained from experiments).

![Figure 6](image.png)

**Figure 6.** Predicted $d(\log \sigma)/d\phi$ (from the model) versus actual $d(\log \sigma)/d\phi$ (from experiments).

Both the $R$-squared and adjusted $R$-squared of the regression line depicted in Figure 6 are equal to 1.0000, which indicate that there is a very good agreement between the experimental and predicted values. The calculated standard deviation of the model is $1.828 \times 10^{-3}$. This value is very low, and it implies that the predicted values of $d(\log \sigma)/d\phi$ are very close to the experimental values.

Another statistical parameter used in this work to evaluate the empirical model is adequate precision, which measures the signal-to-noise ratio. The adequate precision was found to be $16956.478$. Since the value is higher than 4, the precision is considered desirable. The high value of adequate precision of the model indicates an adequate signal.

However, not all of the above statistical parameters are sufficient to resolve the accuracy of the model. Thus, the model graph, which is a diagnostic plot, was also investigated. Figure 7 shows the OFD model graph within the whole studied range. It can be seen in Figure 7 that the model is not able to predict the
value of $d(\log \sigma)/d\phi$ within the water content range of 0.02 to 0.07 perfectly because it leads to some negative values, which is practically impossible.

In DOE, statistical analysis and/or the diagnostic plots could be improved by applying appropriate transformation to the response data. Square root, inverse, natural logarithm, base 10 logarithm, inverse square root, power, and arcsine square root are the available transformations in OFD of Design Expert software. Therefore, in order to modify the model, all the transformations were separately implemented on the model. In addition, the statistical parameters as well as the OFD model graphs have been investigated. It was found that, among all transformations, only natural logarithm and power transformations are applicable because the resulting transformed models were significant. It was not true for other transformations. Design Expert software recommends the most appropriate lambda value for the power transformation in one of its plots called Box-Cox plot. Lambda is the power raised by the response in power transformation analysis. The suggested lambda for the power transformation was 0.98. Thus, the natural logarithm transformation and power transformation with lambda value of 0.98 was imposed on the model. Figures 8 and 9 show the OFD model graphs for the transformed models of power and natural logarithm, respectively.

Figure 8 shows the modified model with power transformation, which is again unable to be predicted in a water content interval between 0.02 and 0.07. Since $d(\log \sigma)/d\phi$ against $\phi$ is a continuous function, power transforming of the model seems to be invalid.

The OFD model graph shown in Figure 9 indicates that natural logarithm transformation seems to be the best possible transformation in the modeling. Therefore, the final empirical model in terms of the actual factor can be expressed as follows:

$$\ln(d(\log \sigma)/d\phi) = +3.41324 - 178.28185\phi + 3663.79302\phi^2 - 24292.25136\phi^3 + 51385.18915\phi^4$$

(4)

The predicted $d(\log \sigma)/d\phi$ (derived from the final transformed model) versus actual $d(\log \sigma)/d\phi$ (obtained from experiments) is presented in Figure 10. Both the $R$-squared and adjusted $R$-squared of the regression line depicted in Figure 10 are equal to 1.0000. This indicates that there is excellent agreement between the experimental and predicted values from the model. The calculated standard deviation of the model is
3.025 \times 10^{-4}. A very low value of standard deviation implies that the predicted values of \( d(\log \sigma)/d\phi \) are very close to the experimental values. Finally, the adequate precision was found to be 9272.721, which is relatively high, and it indicates an adequate signal. Therefore, the final transformed model, presented in eq 4, is able to capture a precise correlation between \( d(\log \sigma)/d\phi \) and \( \phi \).

### 3.4.2. ANOVA

The powerful statistical analysis of ANOVA was used to check the adequacy of the model. ANOVA results are given in Table 5. The Model \( F \)-value of 13 580 914.78 implies that the model is significant. There is only 0.01% chance that a "Model \( F \)-Value" in such high magnitude could occur due to noise. The \( p \)-value (or Prob > \( F \)) of the model is less than 0.0001, which confirms that the model is significant. In addition, the ANOVA table also shows that all of the model parameters are significant because their \( p \)-values are less than 0.05.

### 3.4.3. Optimization

The main objective of this study is to show the capability of DOE in estimating water percolation threshold \( (\phi_c) \). To fulfill this objective, the final quadratic model of the \( d(\log \sigma)/d\phi \) with \( \phi \) was numerically optimized to determine the water volume fraction at which the \( d(\log \sigma)/d\phi \) is at a maximum. After setting the goal factor and the goal response to "within the range" and "maximize", numerical optimization was carried out using Design Expert software. The summary of the optimization is tabulated in Table 6. It was computed that, at water volume fraction of 0.1245, \( d(\log \sigma)/d\phi \) reaches its highest value of 32.2584. Thus, the predicted value of \( \phi_c \) from DOE is 0.1245. This value is in good agreement with the predicted value of \( \phi_c \) from fitting to the scaling law, which was 0.1212. The very low error percent of 2.7% confirms the capability of the DOE in predicting \( \phi_c \) of a microemulsion.

### 3.4.4. Rationalization of the Conductance Mechanism

"Hopping" and "transient fusion-mass transfer-fission" are the two mechanisms, which have been proposed and widely explained in the literature to describe the occurrence of conductance percolation in various w/o microemulsion systems.\(^{31−34}\) The predicted functions of the electrical conductivity (\( \sigma \)) and its logarithm (\( \log (\sigma) \)) for the studied microemulsion system were obtained from the final statistical model in eq 4. These functions are shown against the water content (\( \phi \)) in Figure 11. It demonstrates that the electrical conductance is very low (relatively zero) when the water content of the microemulsion is below the water percolation threshold.

<table>
<thead>
<tr>
<th>parameter</th>
<th>goal</th>
<th>lower</th>
<th>upper</th>
<th>optimized condition</th>
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<tr>
<td>water volume fraction</td>
<td>in range</td>
<td>0.0225</td>
<td>0.2018</td>
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<td>( d(\log \sigma)/d\phi )</td>
<td>maximize</td>
<td>2.6991</td>
<td>28.8908</td>
<td>32.2584</td>
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</table>

Figure 10. Predicted \( d(\log \sigma)/d\phi \) (from the final transformed model) versus actual \( d(\log \sigma)/d\phi \) (from experiments).

Figure 11. Predicted electrical conductivity and its logarithm at various water contents.

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Table 6. Summary of Optimization for the Final OFD Modeling

<table>
<thead>
<tr>
<th>parameter</th>
<th>goal</th>
<th>lower</th>
<th>upper</th>
<th>optimized condition</th>
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<td>water volume fraction</td>
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<tr>
<td>( d(\log \sigma)/d\phi )</td>
<td>maximize</td>
<td>2.6991</td>
<td>28.8908</td>
<td>32.2584</td>
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Table 5. ANOVA Table

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<tr>
<th>source</th>
<th>sum of squares</th>
<th>df</th>
<th>mean square</th>
<th>( F ) value</th>
<th>( p )-value Prob &gt; ( F )</th>
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<tr>
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threshold. It suggests that, below the water percolation threshold, the individual water droplets in the w/o microemulsion behave like large isolated molecules in solution without any interdroplet interaction. The statistically predicted functions in Figure 11 also show that, above the water percolation threshold, the electrical conductance increases sharply.

The results shown in Figure 11 support the conduction mechanism involving transient fusion and mass exchange. According to this mechanism, an effective collision between two water droplets in a w/o microemulsion is essential for the water droplet to fuse together, aggregate into clusters, and form an open structure for the efficient transport of Na\(^+\) ions. NaCl is an electrolyte, which contributes to the conductivity of the system. The addition of NaCl to the nonionic microemulsion raises the Na\(^+\) concentration in the water droplets. The dissolved Na\(^+\) in water is transported from one droplet to another by mass exchange technique upon droplet fusion. The mass exchange between the fused droplets plays an important role in the sharp increase of electrical conductance at water percolation threshold. The IPA used in the formulation of the microemulsion is also considered a fair medium for ionic conduction. Therefore, the presence of IPA in microemulsion structure facilitates the process of ionic conductance, and therefore, Na\(^+\) ions can move freely between the fused droplets.\(^2\)

4. CONCLUSIONS

In this study, DOE was used to model d(log \(\sigma\))/d\(\phi\) as a function of \(\phi\) to show the possibility of the use of DOE in prediction of water percolation threshold for a specific system diluted along a specific water dilution line. In DOE modeling, a quadratic equation has successfully been fitted to electrical conductance data along a specific dilution line. To improve the prediction of the model, natural logarithm transformation was implemented. The results in the ANOVA table showed that the final transformed model and all coefficients are significant. A statistical parameters study also showed that the final model is very precise. The final model was then used to estimate the value of \(\phi_p\) for a microemulsion by maximizing d(log \(\sigma\))/d\(\phi\) within the whole range of \(\phi\). The predicted value from DOE was 0.1245, which was very close to the predicted value obtained from the fitting of the scaling law (0.1212). It is concluded that DOE could be used as an alternative and reliable method in predicting \(\phi_p\) with less restriction and computation compared to the conventional fitting method.

**REFERENCES**


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**Notes**

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