Manuscript Number:

Title: Prediction of Water and Oil Percolation Thresholds of a Microemulsion by Modeling of Dynamic Viscosity using Design of Experiments

Article Type: Full Length Article

Section/Category: Colloid and Interface Chemistry

Keywords: design expert; microemulsion; percolation threshold; viscosity.

Corresponding Author: Dr. Badrul Mohamed Jan,

Corresponding Author's Institution: University of Malaya

First Author: Zahra Jeirani

Order of Authors: Zahra Jeirani; Badrul Mohamed Jan; Brahim Si Ali; Ishenny Mohd Noor; Chun Hwa See; Wasan Saphanuchart

Abstract: This paper presents the application of Design of Experiments to predict water and oil percolation thresholds of a microemulsion using dynamic viscosity data as a function of water volume fraction. One-factor and historical data were the two investigated design types of response surface methodology. The models were validated and maximized. The predicted water and oil percolation thresholds using historical data design were close to their experimental values. The oil percolation threshold could be predicted more precisely using one-factor design than historical data design while one-factor design can capture the relationship between the response and design factor with fewer experimental data.

Suggested Reviewers: Saeid Baroutian
New Zealand Forest Research Institute
s.barout@gmail.com

Monzer Fanun
Al-Quds University
Fanunn@gmail.com; mfanun@science.alquds.edu

Ali Mohebbi
University of Adelaide
amohebbi2002@yahoo.com
Prediction of Water and Oil Percolation Thresholds of a Microemulsion
by Modeling of Dynamic Viscosity using Design of Experiments

Zahra Jeirani a, Badrul Mohamed Jan a*, Brahim Si Ali a, Ishenny Mohd Noor a, See Chun Hwa b, Wasan Saphanuchart b

a Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

b BCI Chemical Corporation Sdn. Bhd., Lot 7, Jalan BS 7/22, Taman Perindustrian Bukit Serdang, Seksyen 7, 43300 Seri Kembangan, Selangor Darul Ehsan, Malaysia

ABSTRACT

This paper presents the application of Design of Experiments to predict water and oil percolation thresholds of a microemulsion using dynamic viscosity data as a function of water volume fraction. One-factor and historical data were the two investigated design types of response surface methodology. The models were validated and maximized. The predicted water and oil percolation thresholds using historical data design were close to their experimental values. The oil percolation threshold could be predicted more precisely using one-factor design than

* Corresponding author, Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia, Tel.: +60379676869; Fax: +60379675319; E-mail address: badrules@um.edu.my (Badrul Mohamed Jan).
historical data design while one-factor design can capture the relationship between the response and design factor with fewer experimental data.

**Keywords:** design expert; microemulsion; percolation threshold; viscosity

1. **Introduction**

Microemulsions are dispersions of oil and water stabilized with an appropriate surfactant(s). They are spontaneously formed, thermodynamically stable, and optically transparent systems with unique properties such as ultra-low interfacial tensions (IFT) [1-3]. Because of their remarkable properties, they have been widely used in several industrial applications including enhanced oil recovery (EOR) [4, 5]. A co-surfactant or a co-solvent is often incorporated in the formulation of a microemulsion to improve the performance and properties of the surfactant [4,5]. Thus mixture of surfactants, specifically mixture of nonionic surfactants has extensively been utilized in industries [3, 6-8] because a mixture of nonionic surfactants is insusceptible to precipitate and it is more effective in lowering the monomer concentration [6, 8].

Phase behavior and microstructure of microemulsion solutions are influenced by the relative amounts of the microemulsion components [9, 10]. Various physical techniques have been applied to elucidate the internal structure of microemulsions. Small angle X-ray scattering (SAXS) [6, 11, 12], small angle neutron scattering (SANS) [11, 12], dynamic light scattering (DLS) [12-14], nuclear magnetic resonance (NMR) [11, 15], time resolved fluorescence quenching (TRFQ) [16], transmission electron microscopy (TEM) [13, 17, 18], electrical
conductivity [2, 6, 14, 15, 19], dynamic viscosity [6, 15, 19], calorimetry [13, 14], infrared spectroscopy [18, 20], cyclic voltammetry (CV) [14], and ultrasonic absorption [19, 21] are some of the common techniques which are applied frequently to provide information on the microstructure of microemulsions.

Dynamic viscosity measurements evidenced that the overall geometry of the particles of the dispersed phase in microemulsion depends on the amount of solubilized water [9]. In addition, experiments showed that the variation of dynamic viscosity as a function of water volume fraction reflects the microstructural transitions in the microemulsion systems [6, 8, 9, 22, 23]. The microstructural transition points are called water and oil percolation thresholds. One or both of the percolation thresholds have successively been determined by rheological measurements [3, 6, 19, 22-24]. Based on the kind of the surfactant and shape of its micelles in oil-continuous and water-continuous microemulsion, different trends were observed in the plot of dynamic viscosity against water content of the microemulsion. Camel-hump structure with double maxima [3, 6, 19, 22-24] and bell-shaped structure with only one maximum [7, 8] are the two typical trends of viscosity curve as the volume fraction of water increases. The maxima are indicative of the water and oil percolation thresholds in a camel-hump structure [3, 6, 22-24]. The viscosity data confirmed that by increasing water volume fraction, the oil-continuous microemulsion transforms into the bicontinuous microemulsion at water percolation threshold (the first peak of viscosity curve), and then the bicontinuous microemulsion transforms into the water continuous microemulsion at oil percolation threshold (the second peak of viscosity curve) [3, 6, 22-24].

Several researchers have studied percolation threshold(s) of a microemulsion by dynamic viscosity measurements when the viscosity curve was similar to a camel-hump [3, 6, 22-24] or
bell-shaped structure [7, 8]. However, Design of Experiments (DOE) can also be used as an alternative in problem solving by applying statistical modeling and optimization [25, 26]. A statistical design has recently been used in microemulsion study [10] but it has rarely been used to optimize dynamic viscosity data in estimating percolation thresholds.

The objective of this paper is to estimate water and oil percolation thresholds using statistical modeling and optimization of a few dynamic viscosity data using DOE. Therefore, one-factor and historical data design types were conducted in the modeling of dynamic viscosity and the models were optimized to determine the percolation thresholds. The results of these models were compared to deduce the most appropriate model, from which the percolation thresholds can be predicted with the highest precision using DOE. Design Expert® software was used to perform different kinds of response surface methodology (RSM).

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, HLB of 11.9, and CMC of 0.073 g/l at 37°C [27]. It was supplied by Cognis (Malaysia) Sdn. Bhd. which is currently part of BASF Chemical Company. In addition, isopropyl alcohol (IPA, A.R. grade) used as the co-surfactant of microemulsion was supplied by LGC Scientific,
Malaysia. Furthermore, glyceryl monooleate (GM) were supplied by Sigma-Aldrich Sdn. Bhd.,
Malaysia. Finally, palm oil was purchased from local markets in Malaysia.

2.2. Microemulsion Preparation and Dynamic Viscosity Measurements

Nonionic surfactant blend was prepared by mixing equal amounts of APG and GM. IPA was
also mixed with the same amount of palm oil to make the oleic solution. De-ionized water with
electrical resistivity of 18.2 MΩ*cm (Sartorius, arium® 611UF ultrapure water system) was used
for the aqueous phase. The initial solution, which was a mixture of 40wt% oleic with 60wt%
surfactant solutions, was diluted with water dropwise and mixed thoroughly. Then the dynamic
viscosity of the microemulsion was measured at each step at constant temperature of
25±0.5°C and fixed shear rate of 210.8 s⁻¹. The instrument used in these rheological studies was a
rotational viscometer (Haake VT550 controlled-rate viscotester, Germany). The viscometer was
equipped with a coaxial cylinder sensor system consists of a set of NV cup and stainless steel
rotor. This set is mechanically and chemically safe for temperatures up to 100°C. The
temperatures of the samples were controlled with a water bath. The dynamic viscosity
measurements were conducted in triplicate and the average of the experimental data was used in
the next steps. A precaution was taken to ensure reproducible and accurate data by setting the
initial shear stress value to zero before starting the equipment.

2.3. Estimation of Water and Oil Percolation Thresholds by Traditional Method
The dynamic viscosity data were plotted against the water content over a wide range from about 0 to around 1 weight fraction. The percolation thresholds were estimated traditionally from the peaks of the plot. The water content at which the first peak occurs indicates water percolation threshold. On the other hand, the water content at which viscosity yield to its second peak indicates oil percolation threshold.

2.4. Prediction of Water and Oil Percolation Thresholds by Optimization using DOE

One of the reliable statistical techniques of DOE to predict the relationship between the response(s) and independent variable(s) is RSM [26, 28, 29]. When a regression model is determined statistically by RSM from few appropriate experimental data, RSM is capable of optimizing the response function and predicting future responses [26]. Design Expert® software version 8.0.7 (STAT-EASE Inc., Minneapolis, USA) was used to conduct RSM. Several design types of RSM are provided by Design Expert software. Box-Behnken, central composite, one-factor, miscellaneous, optimal, and historical data are some of the various design types for RSM in the software.

Selection of design type depends on the number of design factors. In this work, RSM was applied to determine an approximate function between dynamic viscosity of microemulsion and its water content. Thus the water content is the only factor that influences the response, which is dynamic viscosity at constant temperature. When the number of the design factor is one, either one-factor design or historical data design types may be used for the modeling. One-factor RSM design can be applied to find the most appropriate design points when there is only one numeric continuous factor in the experiment. It will be achieved automatically by Design Expert
software. A polynomial model can be developed by one-factor RSM design when the user inserts the experimental response at the design points into the software. However, in historical data RSM design, factor settings and responses of an existing data set can be directly imported to a blank design layout. In this design type, the user defines the design points by using all or some of the available experimental data. Compared to one-factor RSM design, there is no limitation on the number of design factors in a historical data design of RSM.

Both the one-factor and historical data RSM designs were investigated individually to model dynamic viscosity as a function of microemulsion water content. After a model development in all designs, the adequacy of the model was checked using a diagnostic plot called model graph. The verified model was then optimized to estimate the water and oil percolation thresholds.

3. Results and discussion

3.1. Traditional Estimation of Water and Oil Percolation Thresholds using Dynamic Viscosity Data

The measured dynamic viscosity of microemulsions is presented against water volume fraction of microemulsions in Fig. 1. The camel-hump trend of dynamic viscosity with double maxima in Fig. 1 clearly indicates the characteristic of a percolative viscosity model with double percolation thresholds and three microemulsion structures.
Fig. 1. Experimental Dynamic Viscosity of Microemulsions in a Wide Range of Water Contents.

Results of rheological tests showed that the addition of water to a water-in-oil microemulsion (w/o) induces the structure of the system to experience an inversion from w/o to oil-in-water (o/w) over bicontinuous structure at fixed temperature. At initial w/o microemulsion, the water content is close to zero. The dynamic viscosity of this microemulsion was found to be around 160cP. By increasing the water content of the microemulsion, the dynamic viscosity increases gradually and reaches a maximum value of 187cP. The increase of dynamic viscosity within this range of water content indicates attractive interaction and aggregation of water droplets, suggesting molecular reorganization on the interface of the w/o microemulsion occurs [3, 6, 22-24]. The first maximum, which represents water percolation threshold, occurs when the structure of the microemulsion changes from w/o to bicontinuous by percolating water droplets and the appearance of very narrow water channels through the continuous oil phase. Thus it was found experimentally from Fig. 1 that water percolation threshold occurs approximately at water content of 0.0714. Proceeding with further dilution of the bicontinuous microemulsion, the dynamic viscosity of the microemulsion decreases moderately before it starts to increase for the second time. This trend is attributed to the fusion and connection of the narrow water channels, expanding a thicker water channels, and consequently the appearance of greater water networks inside the continuous oil phase [3, 6, 22-24]. With further dilution, the dynamic viscosity of the microemulsion increases until it yields a second maximum value, which indicates an oil percolation threshold. Within this range, very thin oil network loses its continuity and the oil droplet disperses within the continuous water phase [3, 6, 22-24]. Thus the structure of the microemulsion changes from bicontinuous to o/w. Based on the data shown in Fig. 1, the oil
percolation threshold occurs at microemulsion water content of about 0.7743. The sharp decrease in dynamic viscosity of the microemulsion after the oil percolation threshold indicates that the water, which is the least viscous component of the microemulsion system, becomes the continuous phase [3, 6, 22-24].

The experimental water and oil percolation thresholds, which are obtained in this step, are compared to the predicted water and oil percolation thresholds by the application of different design types of RSM in the next steps.

3.2. Prediction of Water and Oil Percolation Thresholds using RSM

3.2.1. Application of One-factor Design

By selecting one-factor design as the design type for the RSM, a regression model for the sole response of dynamic viscosity ($\eta$) was developed as a function of water content ($\phi$). The range of the design factor was divided into two sub-ranges in such a way that each range has only one maximum. Each sub-ranges was used individually for a one-factor design, and therefore two separate regression models were obtained for the dynamic viscosity in these two sub-ranges. The selected minimum and maximum values for the first design sub-range are 0.0189 and 0.7204, respectively. The selected minimum and maximum for the second design sub-range are 0.7204 and 0.9483, respectively. In performing one-factor design as the design type for the RSM, and applying the design sub-ranges, the seven design points were automatically determined by the software for both design sub-ranges individually. The corresponding experimental response values were entered to the model after the seven experiments were performed at the predetermined conditions. The seven experimental conditions and results are tabulated in Tables
1 and 2 for each sub-range. Regression analysis was performed by the Design Expert® software to fit the response function to a quadratic model for each sub-range. An appropriate power transformation was also applied on each of the response data sets to improve the accuracy of the models. The final transformed models in terms of actual factors can be expressed as follows:

\[
(\eta)^{0.37} = +6.64021+1.42198\phi-7.85136\phi^2 \quad 0.0189 < \phi < 0.7204 \quad (1)
\]

\[
(\eta)^{0.36} = +5.23560-12.80500\phi+8.24151\phi^2 \quad 0.7204 < \phi < 0.9483 \quad (2)
\]

Multiple regression analysis technique included in the one-factor design was used in estimation of the coefficients of the models for the response.

Figs. 2(a) and 2(b) show the predicted dynamic viscosity (derived from the one-factor models) versus actual dynamic viscosity (obtained from experiments) at design points at each design sub-range. Both the R-squared and Adjusted R-squared of the regression line depicted in Fig. 2(a) are equal to 1.0000, while the R-squared and Adjusted R-squared of the regression line depicted in Fig. 2(b) are equal to 0.9998 and 0.9997, respectively. The values of R-squared and Adjusted R-squared of both regression lines are very close to one, which indicate excellent agreement between the experimental and predicted values from the models at the design points. The standard deviation of the regression lines in Figs. 2(a) and 2(b) are equal to 8.848×10^{-3} and 1.753×10^{-3}, respectively. The adequate precision of the regression lines in Figs. 2(a) and 2(b) are equal to 530.770 and 211.062, respectively. The low values of standard deviation and the high values of adequate precision show that precise models are achieved.

To further analyze the accuracy of the models, the model graphs were plotted as depicted in Figs. 3(a) and 3(b). The trends of dynamic viscosity predicted by the one-factor designs over both sub-ranges are shown individually. Comparison of Figs. 3(a) and 3(b) with Fig. 1 shows that the predicted trend of the dynamic viscosity model is relatively similar to the experimental
trend depicted in Fig. 1. Therefore, graphical analysis of the models in Eqs. (1) and (2), which are presented in Figs. 3(a) and 3(b), confirm the capability of the models in capturing favorable correlations between dynamic viscosity and water volume fraction of a microemulsion.

**Fig. 2.** Predicted Dynamic Viscosity versus Actual Dynamic Viscosity for One-factor Design with Design Sub-range of (a) $0.0189 < \phi < 0.7204$ and (b) $0.7204 < \phi < 0.9483$.

**Fig. 3.** Model Graph for One-factor Design with Design Sub-range of (a) $0.0189 < \phi < 0.7204$ and (b) $0.7204 < \phi < 0.9483$.

Analysis of variance (ANOVA) was also used to check the adequacy of the one-factor models statistically. ANOVA results are given in Tables 3 and 4 for the first and second sub-ranges, respectively. The Model F-values of 11.78 and 0.067 indicate the models are significant. There is only 0.01% chance that a "Model F-Value" in such high magnitude could occur due to noise. Tables 3 and 4 also show that the p-values (or Prob > F) of the models are less than 0.0001, which confirm that the models are significant. In addition all of the models parameters are significant because their p-values are less than 0.05.

Lack-of-fit is another statistical parameter in an ANOVA table, which is displayed when unnecessary additional design points were used for replication to provide an estimate of pure error [28, 29]. The values of lack-of-fit are reported in Tables 3 and 4 because the models are quadratic, but the design points are seven. Thus five additional design points were used for
replication. Lack-of-fit compares the residual error to the pure error. It is desirable that the parameters of lack-of-fit are insignificant. Based on Tables 3 and 4 the parameters of lack-of-fit are not significant, and the models are able to predict the response.

Both final models of the dynamic viscosity with water content (Eqs. (1) and (2)) using one-factor design were numerically optimized to determine the water volume fractions at which the dynamic viscosity is maximum in each design sub-range. The numerical optimizations of the models using Design Expert software manifest that at water volume fractions of 0.0888 and 0.7769, the dynamic viscosity of the microemulsion yields peak values of 171.173cP and 41.3992cP, respectively. Thus the one-factor design with two design sub-ranges predicts the value of water and oil percolation thresholds to be 0.0888 and 0.7769. Comparison of the predicted water and oil percolation threshold with their experimental values of 0.0714 and 0.7743 shows that with this methodology, the water and oil percolation thresholds can be estimated with error fractions of 0.2437 and 0.0033, respectively. The error values indicate that one-factor design was relatively effective in the prediction of water and oil percolation thresholds with the application of only seven design points.

3.2.2. Application of Historical Data Design

The two sub-ranges of the design factor, produced from the split of the whole range of the design factor, should only involve one maximum. From the application of historical data design in each sub-range, one regression model was acquired individually. Thus a total of two regression models for dynamic viscosity were obtained; each of which is only valid in one of the design sub-ranges. The first design sub-range accommodates the water content data between 0.0189 and 0.7204. The second design sub-range covers the remaining range of water content.
from 0.7204 to 0.9483. Therefore the first 17 experimental data sets in Fig. 1 were used as the design points for the modeling in the first design sub-range. The rest of the experimental data sets in Fig. 1 with additional data set at water content of 0.7204, which is shared in both design sub-ranges, were used as the design points in the modeling within the second design sub-range.

Design Expert® software recommended a polynomial model to be fitted to the response data. An appropriate power transformation was also applied on each of the response data sets to improve the accuracy of the models. The empirical models in terms of actual factors can be expressed as follows:

\[
(\eta)^{0.69} = +35.53419 + 14.87310\phi - 114.25080\phi^2 + 63.39381\phi^3 \\
0.0189 < \phi < 0.7204 \\
\] (3)

\[
(\eta)^{0.28} = +5.39293 - 12.92686\phi + 8.29195\phi^2 \\
0.7204 < \phi < 0.9483 \\
\] (4)

Multiple regression analysis technique included in the historical data RSM design was used in estimation of the coefficients of the model for the response.

Figs. 4(a) and 4(b) show the predicted dynamic viscosity (derived from the historical data models) versus actual dynamic viscosity (obtained from experiments) at design points in each design sub-range. R-squared and Adjusted R-squared of the regression line depicted in Fig. 4(a) are found to be 0.9932 and 0.9916, respectively. R-squared and Adjusted R-squared of the regression line depicted in Fig. 4(b) are found to be 0.9932 and 0.9914, respectively. Since these statistical parameters are approximately close to one, there is relatively good agreement between the experimental and predicted values of dynamic viscosity from the models at the design points.

The model graphs depicted in Figs. 5(a) and 5(b) show the trend of dynamic viscosity predicted by the historical data as a function of water content in each design sub-range separately. The accuracy of the historical data models can be verified with comparing these diagnostic plots
(Figs. 5(a) and 5(b)) with Fig. 1. It was concluded that the trend of the predicted dynamic viscosity obtained from the historical data designs are substantially similar to its experimental trend shown in Fig. 1. Therefore, the models in Eqs. (3) and (4), which are presented in Figs. 5(a) and 5(b), seems to be satisfactorily efficient to be considered as the possible final models of the historical data design.

**Fig. 4.** Predicted Dynamic Viscosity versus Actual Dynamic Viscosity for Historical Data

Design with Design Sub-range of (a) $0.0189 < \phi < 0.7204$ and (b) $0.7204 < \phi < 0.9483$.

**Fig. 5.** Model Graph for Historical Data Design with Design Sub-range of

(a) $0.0189 < \phi < 0.7204$ and (b) $0.7204 < \phi < 0.9483$.

ANOVA was also used to statistically analyze the adequacy of the above models. ANOVA results are given in Tables 5 and 6 for the first and second sub-ranges, respectively. The Model F-values of 628.85 and 580.47 indicate both models are significant. The p-values (or Prob > F) of the models are also reported to be less than 0.0001, which indicate that the models are significant. Furthermore, all of the models parameters are significant because their p-values are less than 0.05.

The final models of the dynamic viscosity with water content (Eqs. (3) and (4)) using historical data design was numerically optimized to determine the water volume fractions at which the dynamic viscosity is maximum in each design sub-range.
The numerical optimizations of the models using Design Expert software elucidate that at water volume fractions of 0.0698 and 0.7803, the dynamic viscosity of the microemulsion yields the peak values of 180.369 and 40.4743cP. Thus the historical data design with two design sub-ranges predicts the value of water and oil percolation thresholds to be 0.0698 and 0.7803 while their experimental values are 0.0714 and 0.7743. The relatively low error fractions of -0.0224 and 0.0077 indicate the reliability of historical data RSM design in prediction of both percolation thresholds. However, the oil percolation threshold could be estimated more accurately by one-factor design using fewer experimental data sets. Therefore, although historical data RSM design found to be adequate in the prediction of both percolation thresholds, it requires more experimental data sets in the modeling than one-factor design. On the other hand, one-factor design showed to be more competent than historical data design in the prediction of oil percolation threshold solely.

4. Conclusions

In this study, water and oil percolation thresholds of a microemulsion were first determined traditionally by plotting experimental dynamic viscosity against water content and finding the water contents at which dynamic viscosity yields the maximum values. The experimental water and oil percolation thresholds were estimated to be 0.0714 and 0.7743, respectively. In addition, two RSM techniques of DOE were used to model dynamic viscosity data as a function of water content statistically. After dividing the range of design factor to two sub-ranges, individual valid models were found in each sub-range of design factor for the two possible design types of one-
factor and historical data. It was concluded that the design type influences the quality of modeling and consequently optimization significantly. It was demonstrated that the error fraction of prediction of water percolation threshold by one-factor and historical data designs are 0.2437 and -0.0224, respectively. Thus historical data design type is considerably more effective than the one-factor design in the prediction of water percolation threshold. It was also determined that the error fraction of prediction of oil percolation threshold by one-factor and historical data designs are 0.0033 and 0.0077, respectively. Although both design types showed to be efficient and reliable in the prediction of oil percolation threshold, one-factor design is more desirable than historical data design because it could estimate the value of oil percolation threshold more precisely using considerably fewer experimental data sets.

**Acknowledgements**

The authors would like to acknowledge the financial support of the Bright Sparks Program at University of Malaya. They also would like to acknowledge the support of University of Malaya IPPP grant, project number: PV021/2011B.

**References**


Table 1

The Conditions of the Seven Runs Determined by the Model for the One-factor Design and their Experimental Response Values ($0.0189 < \phi < 0.7204$).

<table>
<thead>
<tr>
<th>Run</th>
<th>Factor 1: A: water volume fraction</th>
<th>Response 1: dynamic viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.7204</td>
<td>31.7</td>
</tr>
<tr>
<td>2</td>
<td>0.1943</td>
<td>166.3</td>
</tr>
<tr>
<td>3</td>
<td>0.7204</td>
<td>31.7</td>
</tr>
<tr>
<td>4</td>
<td>0.0189</td>
<td>168</td>
</tr>
<tr>
<td>5</td>
<td>0.0189</td>
<td>168.4</td>
</tr>
<tr>
<td>6</td>
<td>0.3696</td>
<td>132</td>
</tr>
<tr>
<td>7</td>
<td>0.5450</td>
<td>80.6</td>
</tr>
</tbody>
</table>
Table 2

The Conditions of the Seven Runs Determined by the Model for the One-factor Design and their Experimental Response Values (0.7204 < ϕ < 0.9483).

<table>
<thead>
<tr>
<th>Run</th>
<th>Factor 1: A: water volume fraction</th>
<th>Response 1: dynamic viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.7774</td>
<td>42</td>
</tr>
<tr>
<td>2</td>
<td>0.8343</td>
<td>30.7</td>
</tr>
<tr>
<td>3</td>
<td>0.7204</td>
<td>31.7</td>
</tr>
<tr>
<td>4</td>
<td>0.7204</td>
<td>31.7</td>
</tr>
<tr>
<td>5</td>
<td>0.9483</td>
<td>6.7</td>
</tr>
<tr>
<td>6</td>
<td>0.8913</td>
<td>16.1</td>
</tr>
<tr>
<td>7</td>
<td>0.9483</td>
<td>6.7</td>
</tr>
</tbody>
</table>
Table 3

ANOVA Table for One-factor Design ($0.0189 < \phi < 0.7204$).

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>Df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>11.78</td>
<td>2</td>
<td>5.89</td>
<td>75256.33</td>
<td>&lt; 0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>A-water fraction</td>
<td>10.63</td>
<td>1</td>
<td>10.63</td>
<td>1.358×10^5</td>
<td>&lt; 0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>$A^2$</td>
<td>1.15</td>
<td>1</td>
<td>1.15</td>
<td>14684.97</td>
<td>&lt; 0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>Residual</td>
<td>3.131×10^-4</td>
<td>4</td>
<td>7.828×10^-5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack-of-Fit</td>
<td>2.960×10^-4</td>
<td>2</td>
<td>1.480×10^-4</td>
<td>17.23</td>
<td>0.0549</td>
<td>Not significant</td>
</tr>
<tr>
<td>Pure Error</td>
<td>1.718×10^-5</td>
<td>2</td>
<td>8.589×10^-6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor. Total</td>
<td>11.78</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 4

ANOVA Table for One-factor Design (0.7204 < ϕ < 0.9483).

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>Df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.067</td>
<td>2</td>
<td>0.033</td>
<td>10831.61</td>
<td>&lt; 0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>A-water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>volume</td>
<td>0.052</td>
<td>1</td>
<td>0.052</td>
<td>17072.04</td>
<td>&lt; 0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>fraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A^2 )</td>
<td>0.014</td>
<td>1</td>
<td>0.014</td>
<td>4591.19</td>
<td>&lt; 0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>Residual</td>
<td>1.229×10^{-5}</td>
<td>4</td>
<td>3.073×10^{-6}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack-of-Fit</td>
<td>1.228×10^{-5}</td>
<td>2</td>
<td>6.140×10^{-6}</td>
<td>928.74</td>
<td>0.0011</td>
<td>Not significant</td>
</tr>
<tr>
<td>Pure Error</td>
<td>1.322×10^{-8}</td>
<td>2</td>
<td>6.611×10^{-9}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor. Total</td>
<td>0.067</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5

ANOVA Table for Historical Data Design (0.0189 < ϕ < 0.7204).

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>1313.30</td>
<td>3</td>
<td>437.77</td>
<td>628.85</td>
<td>&lt; 0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>A-water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>volume</td>
<td>218.11</td>
<td>1</td>
<td>218.11</td>
<td>313.31</td>
<td>&lt; 0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>fraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A²</td>
<td>58.80</td>
<td>1</td>
<td>58.80</td>
<td>84.46</td>
<td>&lt; 0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>A³</td>
<td>4.04</td>
<td>1</td>
<td>4.04</td>
<td>5.80</td>
<td>0.0316</td>
<td>Significant</td>
</tr>
<tr>
<td>Residual</td>
<td>9.05</td>
<td>13</td>
<td>0.70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor. Total</td>
<td>1322.35</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 6

ANOVA Table for Historical Data Design ($0.7204 < \phi < 0.9483$).

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>0.076</td>
<td>2</td>
<td>0.038</td>
<td>580.47</td>
<td>&lt; 0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>A-water volume</td>
<td>0.053</td>
<td>1</td>
<td>0.053</td>
<td>798.28</td>
<td>&lt; 0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>fraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A²</td>
<td>0.015</td>
<td>1</td>
<td>0.015</td>
<td>224.88</td>
<td>&lt; 0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>Residual</td>
<td>$5.262 \times 10^{-4}$</td>
<td>8</td>
<td>$6.577 \times 10^{-5}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor. Total</td>
<td>0.077</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure captions

Fig. 1. Experimental Dynamic Viscosity of Microemulsions in a Wide Range of Water Contents.

Fig. 2. Predicted Dynamic Viscosity versus Actual Dynamic Viscosity for One-factor Design with Design Sub-range of (a) $0.0189 < \phi < 0.7204$ and (b) $0.7204 < \phi < 0.9483$.

Fig. 3. Model Graph for One-factor Design with Design Sub-range of (a) $0.0189 < \phi < 0.7204$ and (b) $0.7204 < \phi < 0.9483$.

Fig. 4. Predicted Dynamic Viscosity versus Actual Dynamic Viscosity for Historical Data Design with Design Sub-range of (a) $0.0189 < \phi < 0.7204$ and (b) $0.7204 < \phi < 0.9483$.

Fig. 5. Model Graph for Historical Data Design with Design Sub-range of (a) $0.0189 < \phi < 0.7204$ and (b) $0.7204 < \phi < 0.9483$. 
May 03, 2012

The Journal Editor
Journal of Industrial and Engineering Chemistry

Dear Editor,

I would like to submit our research paper, which is entitled “Prediction of Water and Oil Percolation Thresholds of a Microemulsion by Modeling of Dynamic Viscosity using Design of Experiments” for consideration for possible publication in Journal of Industrial and Engineering Chemistry. Please kindly receive the original copy of the manuscript as well as the figures, which are uploaded separately.

1. All authors have materially participated in the research and article preparation.
2. The work has not been published previously.
3. It is not under consideration for publication elsewhere.
4. Its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out.
5. If accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Your kind consideration is highly appreciated in advance.

Best regards,

Dr. Badrul Mohamed Jan

Department of Chemical Engineering
Faculty of Engineering
University of Malaya
50603 Kuala Lumpur,
Malaysia.
Tel.: +60-3-79676869
Fax: +60-3-79675319
E-mail: badrules@um.edu.my
Predicted vs. Actual

(a)

Predicted dynamic viscosity (cP)

Actual dynamic viscosity (cP)

(b)

Predicted dynamic viscosity (cP)

Actual dynamic viscosity (cP)
Figure 3

Click here to download high resolution image