Estimation of molecular size of triglyceride in a variety of solvents by using the intrinsic viscosity technique: an important index for transesterification of triglyceride in homogenous system

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Abstract. The effect of solvent type on the molecular size and intermolecular interaction of triglyceride was investigated by the intrinsic viscosity technique. Both the indices may be important for discussing and scrutinizing the behavior of homogeneous transesterification of triglyceride with alcohol since it was found that the co-solvent type influences both the transesterification rate and hydrodynamic size of triglyceride in a homogeneous system. Kinematic viscosity of palm oil dissolved in six different solvents was measured at 298 K by using glass capillary type viscometer to determine the intrinsic viscosity and Huggins constant. By plotting the intrinsic viscosity and Huggins constant against the seven physical properties of the solvents, the polarity of the solvent has been identified as the key factor for molecular size of triglyceride in solution. On the contrary, none of the seven physical properties showed good correlation with the Huggins constant. This may be attributed to more complex nature of the Huggins constant in comparison with the intrinsic viscosity.

1. Introduction
In a previous study, the authors found that the type of co-solvent influenced the reaction rate of homogeneous transesterification of triglyceride catalyzed by alkaline catalyst [1]. We also found that the molecular size of triglyceride in solution is different in methyl ethyl ketone (MEK) and tetrahydrofuran (THF) [2]. We hypothesized this size change may influence the homogeneous transesterification rate of triglyceride. To refine and prove this hypothesis, it is important to understand how the solvent type influences the molecular size of triglyceride in solution. From this viewpoint, we empirically investigated the effect of solvent type on the size of triglyceride by using the intrinsic viscosity technique in the present study. In this technique, the viscosity of oil dissolved in the solvent at several different concentration levels was measured in order to obtain the intrinsic
viscosity and Huggins constant. The former is an index of the solute molecular size. The latter is an index of inter-solute interaction [3]. Palm oil was used as triglyceride. Two alcohols (1-propanol and 1-butanol), two ketones (acetone and MEK) and one ether (THF) were used as solvents. We also report what physical property of the solvents determines the size and interaction of triglyceride in solution.

2. Materials and Methods
The materials used in this study are all commercially available. Palm oil is of cooking oil grade (Seri Murni Brand) and was purchased from a local shop. Five types of reagent grade solvent; 1-propanol, 1-butanol, acetone, MEK and THF were used. The kinematic viscosity of solvents and solutions was measured by a reverse flow capillary viscometer. The density of solvents and solutions was measured by a glass made Pycnometer. Solutions of palm oil in different solvents were prepared at four levels of concentration between 0.05 and 0.17 g/mL. Their density and kinematic viscosity were measured at 298 K. The viscosity \( \eta \) was calculated by multiplying kinematic viscosity by density. The relative viscosity \( \eta_r \) is defined by the following equation:

\[
\eta_r = \frac{\eta_{\text{(solution)}}}{\eta_{\text{solvent}}} \tag{1}
\]

The relative viscosity \( \eta_r \) was plotted against the concentration \( c \) in order to obtain the two parameters, the intrinsic viscosity \( [\eta] \) (mL/g) and Huggins constant \( k' \) (dimensionless), based on the following theoretical equation [3]:

\[
\eta_r = k'[\eta]^2c^2 + [\eta]c + 1 \tag{2}
\]

where \( c \) is the concentration of solute (g/mL). It is well known that the intrinsic viscosity is proportional to the third power of the hydrodynamic size of solute molecule in solution as shown in Eq (3), and the Huggins constant an index for interaction between adjacent solute molecules [3].

\[
[\eta] = \frac{10}{3} \pi N_A R^3 \frac{1}{M} \tag{3}
\]

where \( N_A \) is the Avogadro number, \( R \) the hydrodynamic radius of the solute, \( M \) the molecular weight of the solute. This equation can be re-arranged to obtain Eq (4), from which the hydrodynamic radius of oil can be calculated.

\[
R[\text{nm}] = 0.05413([\eta]M)^{1/3} \tag{4}
\]

3. Results and Discussion
The intrinsic viscosity and Huggins constant for palm oil solutions obtained in this study are tabulated in Table 1.

| Solvent                          | Intrinsic viscosity (mL/g) | Huggins constant (-) |
|---------------------------------|---------------------------|-----------------------|
| Tetrahydrofuran (THF)           | 4.14                      | 0.719                 |
| Methyl ethyl ketone (MEK)       | 3.63                      | 0.951                 |
| Acetone                         | 3.11                      | 1.689                 |
| 1-Propanol                      | 2.44                      | 1.019                 |
| 1-Butanol                       | 2.23                      | 0.863                 |
The theory says that the intrinsic viscosity is a good index to represent the molecular size of a solute dissolved in the solution. This has been empirically authorized already in the field of polymer. On the other hand, in the field of rather lower molecular weight, such as triglyceride, it has not been well supported by accumulated data. However empirical evidence is being accumulated recently as follows. A previous paper [4] reported that the intrinsic viscosity of 2.7 g/mL for coconut oil (MW=658) was smaller than 3.3 g/mL for palm oil (MW=851) in MEK at 298 K. The same trend was also observed for different solvent THF in the paper. Igwe [5] measured the intrinsic viscosity of some vegetable oils at different temperatures. Their values range from 4 to 13 mL/g, which are a little higher than what we obtained. But if we take into account the fact that their solvents (BTX and C4-C6 alcohols) are different from what we used, this difference may not be a big issue. They observed temperature dependence of the intrinsic viscosity and attributed this to cluster formation. This kind of cluster formation was also proposed by Takashima [6] for chlorophyll. This cluster formation hypothesis sounds relevant to Takashima’s results since their intrinsic viscosity value changed approximately 1000 times by condition change. On the other hand, Igwe [5] observed only 2 to 3 times difference. Thus, their cluster formation scheme maybe still a little questionable. Anyway none of them [5,6] estimated the size of cluster from the intrinsic viscosity. The size can be estimated by using Eq. (4) as we did.

The results in Table 1 obviously shows that both the parameters the intrinsic viscosity and Huggins constant, vary depending on the type of solvent. The question now is what property of solvent relates to these two parameters. To answer this question, the intrinsic viscosity and Huggins constant are plotted against various physical properties [7] of the solvents used in this study in Figures 1 and 2, respectively. From Figure 1, the solubility in water and relative polarity seem to be well related to the intrinsic viscosity. Figure 2 shows that none of the physical properties applied show good linear correlation with the Huggins constant, which may have more complex nature than the intrinsic viscosity [8]. To make this point more quantitative, the $R^2$ of linear regression is tabulated in Table 2.

![Figure 1](image-url)  
**Figure 1.** The physical property of solvents vs. intrinsic viscosity
As shown in Table 2, solubility in water and relative polarity show a strong linear correlation with intrinsic viscosity. But solubility of water may not be a relevant candidate since there are only three out of the five solvents as shown in Figure 1(a). The missing two, acetone and 1-propanol, are miscible with water. Therefore, relative polarity is chosen as the most suitable physical property for intrinsic viscosity. This fact can be interpreted by a scheme illustrated in Figure 3. A solvent with lower polarity, such as THF and MEK, may have a higher affinity to the three alkyl groups of triglyceride, and therefore can move into the spaces in entangled alkyl chains easily. This may result in expansion of alkyl group, and hence increase the hydrodynamic size of triglyceride.

**Table 2. Values of $R^2$ for the plot in Figures 1 and 2**

| Physical property       | $R^2$ for intrinsic viscosity (mL/g) | $R^2$ for Huggins constant (-) |
|-------------------------|-------------------------------------|--------------------------------|
| Boiling point (°C)      | 0.566                               | 0.240                          |
| Melting point (°C)      | 0.016                               | 0.025                          |
| Density (g/mL)          | 0.415                               | 0.458                          |
| Solubility in H$_2$O (g/100g) | 0.995                               | 0.100                          |
| Relative polarity       | 0.936                               | 0.000                          |
| Elution strength        | 0.615                               | 0.009                          |
| Vapor pressure at 20°C (hPa) | 0.406                               | 0.286                          |

Figure 4 shows the hydrodynamic radius of oil molecule in solution (blue bars) in the decreasing order from left to right, together with the Huggins constant (orange bars). From the following relationship between the pure oil density $\rho$ and the equivalent radius of pure oil $R_{\text{pure}}$ (Eq. (5)), Eq. (6) can be derived.
\[ \rho = \frac{M}{3\pi R^3 N_A} \]  

\[ R_{\text{pure}}[\text{nm}] = 0.07346 \left( \frac{M}{\rho} \right)^{1/3} \]

**Figure 3.** Effect of solvent polarity on the size of the triglyceride molecule

Non-polar solvent molecules easily move into entangled alkyl groups of triglyceride. 
Alkyl groups expand. 
Higher intrinsic viscosity.

Polar solvent molecules can’t move into entangled alkyl groups of triglyceride. 
Alkyl groups stay at a smaller size. 
Lower intrinsic viscosity.

**Figure 4.** Hydrodynamic radius and Huggins constant of palm oil- various solvent systems

![Graph showing hydrodynamic radius and Huggins constant for different solvent systems](image-url)
From Eq. (6), $R_{pure}$ is obtained as 0.722 nm, which is the closest to the hydrodynamic radius of triglyceride in acetone. This may be rephrased to:

1. Acetone causes little expansion or contraction of oil molecules or has a neutral effect on the oil molecular size.
2. THF and MEK may have a positive effect or result in expansion of oil molecules.
3. 1-Propanol and 1-butanol may have a negative effect or result in contraction of oil molecules.

This trend is also consistent with the fact that acetone has the highest Huggins constant, or allows oil molecules to have the maximum oil-oil interaction.

Since, to the authors’ knowledge, calculation of oil molecular size from the intrinsic viscosity by applying Eq. (4) has not been reported, further discussion for the relevancy of this technique is a little difficult. But it is noteworthy to point out the fact that the size of the dissolved oil molecule in Figure 4 (0.7-0.8 nm) is quite close to the one estimated from the density by applying Eq. (6) (0.722 nm).

4. Conclusion
The viscosity of oil dissolved in different solvents was measured in order to obtain the intrinsic viscosity, an index for solute molecular size, and Huggins constant, an index for interaction among adjacent solutes. Both the indices were influenced by solvent type. This paper suggested that these phenomena are primarily controlled by solvent polarity.

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