

An Estimation Method for the Viscosity of Dissolved Waxy Lube Oils in MEK-Toluene Solvent Composition

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ABSTRACT: This paper presents a general inspection method of the dynamic viscosity of lubricating oil feedstock dissolved in MEK/toluene in solvent dewaxing process, where the higher normal paraffin components are to be extracted. A reliable technique to determine the flow properties in the complex multi-components mixture depends on selection of higher carbon number as a solute and light one as a liquid that matches the wax mass fraction in the light portion of the oil. The study focuses on the viscosity in the dissolution region (liquid phase) as a starting point to characterize the solution behavior. The tested feed stock is ASE 30 and the solvent is MEK-Toluene. The selected high carbon numbers are C₃₃, C₃₄, and C₄₅, while the light one is C₁₀. The obtained viscosity results by the proposed method were found to be in good agreement with the predicted viscosities of multi mixture components using the available mixed rules in the literature. The results showed that the proposed solubility model could govern the characteristics of the lubricating base stock oil in dissolution region based on the selected carbon number.

Key words— Carbon number, Crystallization, Dewaxing, Dissolution region, Lube oil, Multi components dynamic viscosity, Solubility model, Solvent dewaxing process, Waxing.

INTRODUCTION

The lube oil base stocks are prepared from selected crude oils by distillation and special processing in order to meet the desired qualifications, (Sequerira 1994). These petroleum products possess high viscosity that they become sticky at low temperatures. The main reason is due to longer chain length of paraffinic hydrocarbons in those products, which restrict the

flow, (Thomas 2008). The solvent which are normally used to ease the flow of the lube oil are Methyl Ethyl Ketone (MEK) combined with aromatic component, such as toluene. The major steps in preparing the feedstock charging with MEK dewaxing unit can be broken down into two processes, namely premixing the feed with a reasonable ratio of MEK and toluene to avoid oil immiscibility and heating the feed/solvent mixture above the cloud point to dissolve any wax microcrystals, (Thomas 2008). The lube oil feedstocks consist of multi component mixtures of cycloparaffins, linear paraffins and a small amount of aromatics components. However, most crystallization leading to solidification is attributed to the linear paraffins (n-alkanes) because these components have higher pour points than the others components, (Taylor and McCormack 1992). Therefore, the solvent dewaxing process is only used to remove the heavier normal paraffins. The experimental methods used for determination of lube oil feedstock characteristics in solvent dewaxing process are very limited, because these processes are confidential to the petroleum industry companies. The published studies that are related to the phenomena of this work have investigated the viscosity of the oil-MEK-toluene mixture by experimental measurements. Gureev and Klimenko, 1980 investigated experimentally the relative viscosity (ratio of suspension viscosity to the liquid phase viscosity) of three samples of residual raffinates (SAE, motor oil and MS-20) miscible with different solvent (MEK/toluene) volume ratio. Their experimental analysis led to an approximation expression for SAE and motor oils data in a third degree polynomial equation connected to the relative viscosity as a function to the solid wax suspension. The polynomials coefficients differ from each other were depending on the dilution ratio and the raffinat structural nature. The experimental results showed a Newtonian liquids behavior of these samples diluted with solvent volume ratio extended from 2:1 to 5:1.

The view of this work is built on the numerical model done by Li *et al.* 2008 on a pilot plant of solvent dewaxing using the MEK/toluene as a solvent. Imai *et al.* 2001 have demonstrated that the mostly presence of carbons in the paraffinic wax are C_{24} , C_{28} or C_{32} . Li et al 2008 assumed that the solute wax could be represented by higher carbon number of C_{24} , C_{28} or C_{32} using the solubility model formula. The predicted viscosity of the liquid solution was determined using logarithm mixed rules by neglecting the interaction of the solvent and oil, assuming a homogenous solution.

From above literature, it can be released that there is no deliberation to compare the experimental measured liquid viscosity in the dissolution region of the lube oil feedstock and

the results of liquid viscosity predicted from theoretical data using mixed rules with the representative chosen carbon number for the oil portion.

The objective of this paper is to present a method of the viscosity prediction of the waxy oil-solvent mixture in the dissolution region (liquid phase). The process of characterizing the lube base oil in solvent dewaxing includes:

- Investigation of the higher carbon number of n-paraffin to represent the solid dissolved wax and the light carbon number as a solution using the solubility prediction model.
- Measurement and prediction of the dynamic viscosity of oil-wax-solvent mixture as a multi organic mixture in dissolution region using mixed rules and the available empirical formula for each single component.

EXPERIMENTAL MEASUREMENTS

The experimental investigations have been carried out utilizing a sample of residual waxy lube oil feedstock, SAE30 which was distilled in Melaka refinery - Malaysia.

Differential Scanning Calorimetry Test

Thermal analyses was performed using Mettler DSC apparatus, consisting of a measurement unit for setting and measuring the sample, and a base unit for processing the signals that were originated from the measurement unit. The acquired data were sent to the data acquisition software for analysis. The two measurement chambers of the DSC are designed to measure the heat flux.

The preparation work for the sample consisted of several stages. The sample was firstly heated to 80 °C and then shaken to ensure a complete dissolution and homogeneity, and was kept for about 24 hours to eliminate the thermal history. A sample of 7.88 mg of the lube oil specimen was loaded into an aluminum pan, which was then sealed and weighed. Experiments were carried out by heating two pans: one for the sample and the other blank one for a reference at 80 °C. The sample were then cooled from 80 to -80 °C using liquid-nitrogen with a cooling-rate of 5 °C/min, and then heated up in the same temperature range. To predict the wax content using the thermal analysis of the DSC scan, the method developed by Chen et al 2004 was adopted. The method was used to compute the total thermal heat released during

wax crystallization in exothermic process. The prediction could be done by integrating the area under the deflection curve between the onset crystallization temperature and -20 °C on the reference base line as shown in Fig.1.

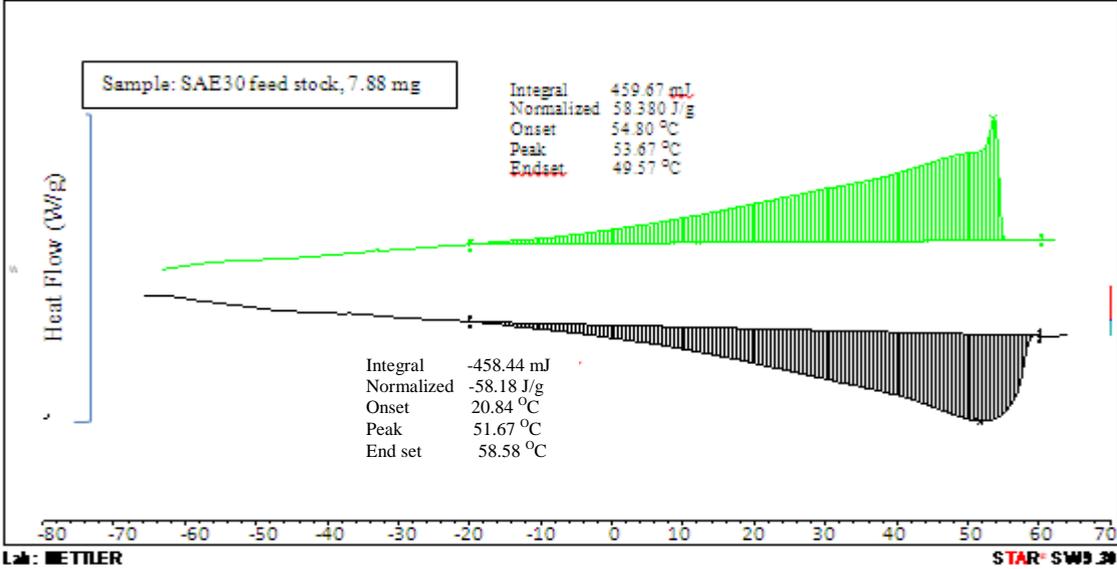


Fig. 1 DSC thermal analysis of lube oil feedstock

Chen *et al.*, 2004 have derived an empirical formula which combined the heat released and the wax content. The formula could predict the wax content from the total heat, and it is represented as follows:

$$w_w = 0.75Q + 0.2 \tag{1}$$

where,
 w_w (wt.%) wax content, and
 Q is the total heat in (J/g).

The wax mass fraction of the feedstock and the dissolution temperature were found to be 43.95 (wt %) and 58.6 °C, respectively.

Viscometry test

Most of the previous studies that addressed the rheology of the waxy paraffin crude oil and their products ensured the alteration of the flow behavior from Newtonian to non-Newtonian characteristics after wax crystals appearance has been commented by previous investigators,

e.g., Gureev and Klimenko 1980, Li *et al.* 2008, Imai *et al.* 2001, and Langhame *et al.* 1985. As the flow temperature decreased below the wax appearance temperature (WAT), the concentration of the higher n-paraffin solute in the solution shifted from saturation to supersaturation process.

In the solvent dewaxing unit, the light n-paraffin components combined with MEK/toluene are usually considered as solvents to the higher components in the feedstock mixture, (Pedersen and Ronningsen 2000).

In the present investigation, three ratios of solvent to feedstock which are: 0.7/1, 1/1 and 1.5/1 with 1/1 MEK/toluene solvent ratio have been prepared. The rheological behavior of the three samples was tested by a Couette coaxial cylinder viscometer model 1100 linked with ORCADA™ Software control system. The viscometer is combined with a thermo bath using for heating and cooling the sample at specified thermal rating.

The viscosity measurements was carried out by heating the oil sample to the preheating temperature and kept for 24 hours for thermal history treatment. The sample was then loaded into coaxial cylinder and heated to a desired temperature, then cooled at 1.0° C/min cooling rate.

RESULTS AND DISCUSSION

The procedures used in the research were much dependent on the experimental measurements of the carbon number distribution in the feed stock, dissolved temperature, onset crystallization temperature and wax content. The solubility model was used to estimate of the carbon number existed in the solid wax and in the liquid portion which attached the wax content and dissolving temperature of the feedstock.

Experimental results

Fig. 2 shows the experimental measurements of the viscosity for the three ratios of solvent to feedstock which are: 0.7/1, 1/1 and 1.5/1 with 1/1 MEK/toluene solvent ratio. The graph illustrates the absorption effect, due to the solvent addition, on the flow behavior, which become close to a suspension dispersed system of the higher n-paraffin particles after the measured crystallization temperature. The rapid increase in the measured dynamic viscosity is due to the reduction of the solvent capacity.

This incremental increase of solvent ratios explains the reason of using multi injection dilution points in solvent dewaxing units. The aim is to adjust the viscosity and minimize the pressure drop and solute super-saturation in the mixture flow, (Li and Zhang 2003).

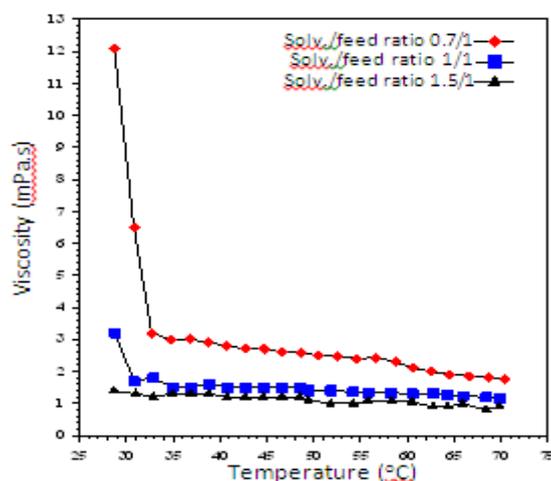


Fig. 2 Measured viscosities at different solvent/feedstock ratios

Solubility model

The solubility is a very important characteristic in the solvent dewaxing because the phase equilibrium of the solid diluted in solution satisfies the required super-saturation. Normally the range of the carbon number distribution of n-alkanes in waxy paraffinic oil is extended from C₂₀ to C₄₀. But the studies have demonstrated that the components which form a single orthorhombic solid solutions are C₂₄, C₂₈ and C₃₀ or C₃₂, e.g., Pedersen and Ronningsen 2000, Ramirez-Gonzalez *et al.* 2009, and Dirand *et al.* 1998. As the solubility prediction of such multi component mixture solution is complex, it is convenient to choose light n-alkanes, as Decane (C₁₀) that can be treated as a single component, (Pedersen and Ronningsen 2000). By using solubility model, it is possible to investigate the mass fraction and dissolving temperature of the wax in the lube base stock oil that matches one of the higher carbon numbers. In this work the investigation of solid n-alkanes extended from C₂₄ to C₃₂ dissolved in C₁₀.

The solubility correlation of high n-alkanes dissolved in light component, as used by Claire *et al.* 1987 and Srivastava *et al.* 1997, is:

$$\ln \phi_s = -\frac{\Delta H_m}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) - \frac{\Delta H_t}{R} \left(\frac{1}{T} - \frac{1}{T_t} \right) + 0.5 \ln \left[\phi_s + (1 - \phi_s) \frac{\bar{V}_s}{\bar{V}_l} \right] - 0.5 (1 - \phi_s) \left(1 - \frac{\bar{V}_s}{\bar{V}_l} \right) \quad (2)$$

where, ϕ_s is the volume fraction of solid n-paraffin; R is the universal gas constant, ΔH_m and ΔH_t are the enthalpy of melting and transition of solid alkanes (J/mol), respectively, T_m and T_t are the respective melting and transition temperatures, and \bar{V}_s and \bar{V}_l are the molar volumes of the solid and liquid n-alkanes, respectively. The corresponding mass fraction of the solid n-alkanes w_s can be predicted using Latini *et al.* 2006 expression, as:

$$\phi_s = \frac{w_s \bar{V}_s M_l}{w_s \bar{V}_s M_l + (1 - w_s) \bar{V}_l M_s} \quad (3)$$

where, M_s and M_l are the molar mass of the solid particles and the liquid portion of n-alkanes, respectively. Table1 shows the theoretical prediction of volume and mass fraction of three components C₃₃, C₃₄ and C₃₅ dissolved in C₁₀.

Table1 calculated mass fraction by equation 1

Carbon No.	Decane C ₁₀	
	w _s (wt %)	Abs. deviation
	(wt %)	
C ₃₃	54.55	10.603
C ₃₄	46.83	2.883
C ₃₅	40.55	3.397

Dynamic viscosity model of multi hydrocarbons mixtures

Several mixing rules have been proposed to evaluate mixture transport properties based on the properties of mixture components. As usual, the rules were grouped based on the parameters used to weigh the effect of various compounds. The simplest mixture-viscosity equation based on the organic liquid components fractions can be in the form, (Latini *et al.* 2006):

$$f(\eta_m) = \sum x_i \cdot f(\eta_i) \quad (4)$$

where, $f(\eta_m)$ is the viscosity function, $(\eta, \ln \eta, 1/\eta)$, x_i is the molar fraction of each single component, and η_i is the component dynamic viscosity. For mixture with components that do not differ much in their structure, (Mehrotra et al). 1996 suggested a common equation for liquid hydrocarbons which gave reasonably accurate results, in the form:

$$\eta_m = (\sum x_i \cdot \eta_i^{1/3})^3 \quad (5)$$

For pure n-alkanes between n-C6 and n-C60 plus all mixtures, a simple model that would fulfill both the temperature and composition dependencies is recommended by Asen *et al.* 1990, as:

$$\eta = A \left[\left(\frac{\sum x_i M_i^{(1+p)}}{\sum x_i M_i^p} - M_{H_2} \right) / M_{CH_2} \right]^{(B+C/T)} \quad (6)$$

Equation 6 is applicable for predicting the viscosity of n-alkanes mixture (wax-oil) in the liquid phase. According to Asen *et al.* 1990, the values of the constants A , B , C and p are $3.5992 \cdot 10^{-3}$, 0.35754, 614.0 and 0.43738, respectively. T is the solution temperature in °C. By assuming a homogenous wax-oil-solvent solution, equations 5 and 6 can be combined in order to evaluate the dynamic viscosity of the total solution.

The comparison of predicted dynamic viscosities for three carbon numbers, i.e. C₃₃, C₃₄, and C₃₅ dissolved in C₁₀ combined with MEK/toluene solvent, was conducted using the measured viscosities at three ratios of solvent/feedstock, as shown in Fig. 2. Fig. 3 illustrates the

experimental results and the predicted values at solvent ratio of 0.7/1, for the three carbon number dissolved in Decane (C_{33} , C_{34} , and C_{35} dissolved in C_{10}).

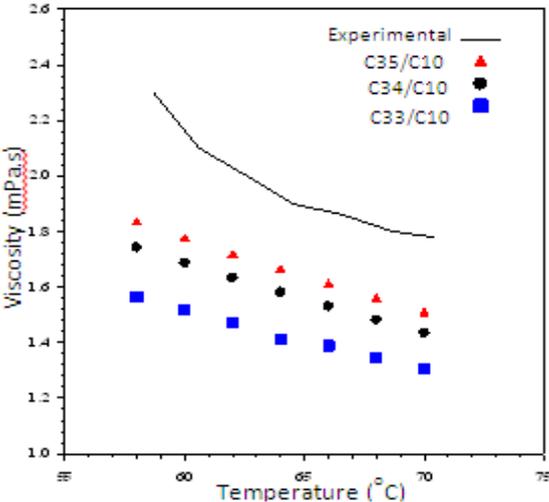


Fig. 3 Measured and predicted viscosities at 0.7/1 solvent/feedstock ratio

From Fig. 4, the predicted results of the viscosity are found to be approximately within around 17% accuracy. It is interesting to highlight that the predicted viscosities for C_{34} dissolved in C_{10} yields a very small deviation (3%) compared to other carbon number. This is in a good agreement with the calculated solubility data.

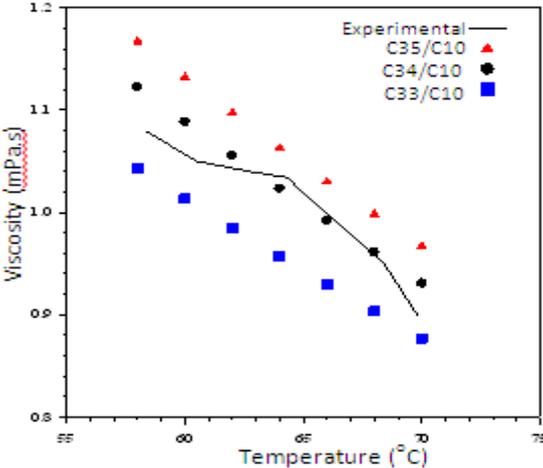


Fig. 4 Measured and predicted viscosities at 1/1 solvent/feedstock ratio.

The deviation between the predicted and the experimental viscosities is smaller when the solvent/feedstock ratio increases to 1.5 for the selected carbon number. This is due to the

highly dilution capacity of the solvent of this carbon number as compared to the others components, as illustrated in Fig. 5.

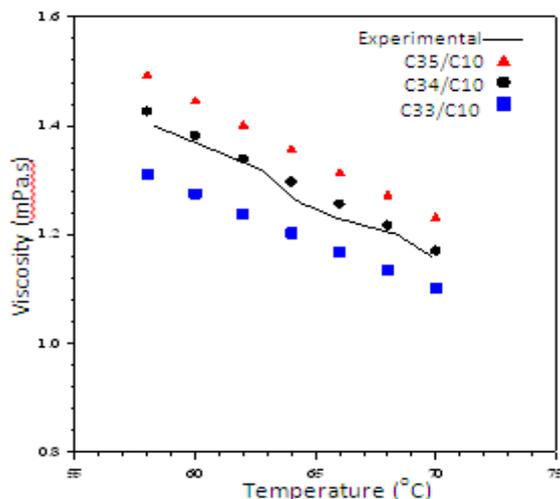


Fig.5 Measured and predicted viscosities at 1.5/1 solvent/feedstock ratio.

CONCLUSIONS

It has been known that dealing with characteristics of the petroleum product such as the lubricating base stock oil is very difficult. The situation becomes more complex in the prediction of the physical properties of the feed dissolved in MEK/toluene that is used in solvent dewaxing, as the flow involves multi mixture organic components. The starting point in this study is to develop a good inspection procedure of the properties in the dissolution region (liquid phase). The solubility model can be used to select the carbon number as the wax representative component.

The predicted viscosities for the chosen carbon number of n-alkanes by this method are in a good agreement with the solubility model prediction.

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