

Prediction of the Kinematic Viscosity of Some Libyan Petroleum Fractions at Different Temperatures

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Abstract—Viscosity is of considerable importance for estimating transport properties in petroleum processing. An adequate knowledge of viscosity plays a very important role in a variety of interesting engineering problems involving fluid flow phenomena and momentum transfer. In this work, experimental data-base consists of density and kinematic viscosity of some distilled petroleum fractions in different boiling temperature ranges derived from Libyan crude oils at several temperature levels (30, 35, 40, 50 °C) are established. Prediction of the kinematic viscosity of liquid mixtures which is based on Eyring absolute rate theory, namely, the McAllister model, has been modified to predict viscosities of undefined liquid mixtures (petroleum fraction) at investigated temperature levels. The results have been validated with the experimental viscosity data gathered in our laboratory. Good agreements between the predicted and experimental values have been observed with an overall average absolute deviation (AAD %) of 3.39 % for McAllister model. The developed model is compared with some widely known viscosity models existed in the literature. The predicted results indicated that the proposed model is much better than predictions made by the literature models.

Keywords—Kinematic viscosity, McAllister model , specific gravity, petroleum fraction.

I. INTRODUCTION

THE viscosity of a liquid is an important physical property that affects the behavior of the liquid as it flows. Highly viscous liquids are more resistant to deformation by stress and flow less easily, while less viscous liquids flow more easily and are less stress-resistant. The two main ways to measure viscosity are in terms of dynamic and kinematic viscosity.

The kinematic viscosity is a major physical property to be used in numerical, experimental and analytical work in all the related fields of fluid flow research. Its determination can be based on experiments with viscometer and on calculations. It measures the resistance of the liquid to flow in the presence of gravity.

Crude oils and their fractions are typically complex mixtures containing predominantly hydrocarbons and undesirable components. For the development, design, planning and operation of processes in the petroleum industry,

an engineer has to deal with the so-called undefined mixtures such as petroleum fractions. The kinematic viscosities of these fractions are required in calculations involving the power requirements for the unit operations such as mixing, pipeline design. A program to experimentally determine the viscosity for all the industrially important materials would be prohibitive in both cost and time. For these reasons accurate correlations of these properties are becoming increasingly important. In general, the viscosity models presently available in the literature are classified into two main categories; viz., predictive and correlative. While the predictive models employ the pure component properties and molecular parameters, the correlative models require costly and time-consuming experimental data (S. Hamzehlouia, A.-F.A. Asfour, 2012).

Many of the studies reported in the literature correlate the viscosity data of petroleum fractions using various empirical mathematical expressions. Of these, the simplest form is the Andrade equation.

$$\ln \eta = A + B/T \quad (1)$$

Where η is viscosity, T is the absolute temperature, and A and B are regressed constants. It is well documented in the literature that the Andrade equation fits experimental liquid viscosity data well (Reid et al. 1987) furthermore, other studies related the regressed parameters to boiling point and API gravity.

In conjunctions with the above method, studies are available in the literature where liquid viscosity calculations were based on Eyring's absolute rate theory such as McAllister model (1960), this model is regarded, by many investigators, as the best available correlative method for binary and ternary regular systems (Reid et al. 1987).

As an extensive literature review shows that, the McAllister model is originally derived to deal with defined liquid mixtures. The applicability of the McAllister model for n-components ($n > 3$) was tested by Nhaesi and Asfour (2000) using regular solution systems. According to the published results, the overall % AAD is 0.75 % for the quaternary; 0.37 % for quinary system.

Al Gherwi et al. (2006) measured and listed the densities and kinematic viscosities of 10 binary regular solutions were measured over the entire composition range at 308.15 and 313.15 K. They used the experimental data to examine the

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predictive capabilities of some viscosity-prediction models; namely, the predictive version of the McAllister model, the GC-UNIMOD model, the generalized corresponding states principle method, and the Allan and Teja correlation. They shows, the results of testing these models revealed that the McAllister model predicts the data much better than the other models and has the lowest absolute average deviation of 1.7%.

Soltani et al.(2010) proposed a generalized equation based on modified Eyring's theory for predicting kinematic viscosity of petroleum fractions. The equation required only molecular weight and boiling point. They used two reference fluids for each range of molecular weights. Nita and Geacai (2011) reported experimental densities and viscosities data for fuels and potential fuels in the range of 20-60 °C and used an empirical equations to predict these properties.

N. Gascoin et al. (2011) proposed a novel measurement method to determine the kinematic viscosity of pure and multi-species fluids, under single phase or supercritical state. It is based on the relationship of Darcy's law in porous media between the pressure drop and the mass flow rate measured through a porous medium.

In this work, experimental data base consists of density and kinematic viscosity of some distilled petroleum fractions in different boiling temperature ranges (160-240°C 160-280°C and 240-340 °C) derived from Libyan crude oils at several temperature levels (30, 35, 40, 50 °C) are established. Then, the McAllister has been modified and used to predict viscosities of these fractions. The results have been validated using the experimental data gathered in our laboratory. Moreover the developed model is compared with some widely known viscosity models existed in the literature such as Amin and Maddox (1980) and Lie *et.al* (1999).

II. EXPERIMENTAL SECTION

To test the proposed models, minimum and maximum viscosity experimental data for investigated range of temperatures of Five petroleum fractions which were distilled from some libyan crude oils into wide and narrow ranges in the laboratory under investigated boiling temperature ranges (three fractions in the range of 160-240 °C , one fraction in the range of 160-280 °C and one fraction in the range of 240-340°C) have been used and reported in Table I. The specific gravities ranges from 0.7791 to 0.8348. Details of the followed experimental technique are documented in Edreder (2004).

Viscosity measurement

The viscometer used herein was a Cannon-Fenske type for transparent liquids (size 50 ranging from 0.8 to 4.0 cSt), immersed in thermostatic bath using water as a medium, the temperature is controlled within 0.01 K. An electronic stopwatch with accuracy of 0.01 s is used to measure the efflux time.

Kinematic Viscosities were obtained from the measured efflux time, t , and the equation:

$$\nu = C t \quad (2)$$

Where ν = kinematic viscosity, mm^2/s , C = calibration

constant of the viscometer (cSt/s) and t = measured flow time, s. The constant was determined by using calibration standards purchased from Cannon Instrument Company.

The kinematic viscosities of these ranges were determined at atmospheric pressure according to ASTM 445 within the selected temperatures levels 30, 35, 40, and 50 °C (Table I). To examine the accuracy of the experiments, the kinematic viscosities for the pure components which are measured herein were compared with the corresponding literature values; it is shown that the reported experimental values of the viscosities conform closely to their corresponding literature values. The results are presented in Table II.

TABLE I
THE EXPERIMENTAL KINEMATIC VISCOSITY (cSt) RANGES AT
DIFFERENT TEMPERATURES (K)

Temperature, K	303.15	308.15	313.15	323.15
Minimum	1.201	1.119	1.047	0.925
Maximum	3.828	3.430	3.090	2.506

TABLE II
EXPERIMENTAL AND REPORTED KINEMATIC VISCOSITIES (cSt) OF N-
ALKANE AT DIFFERENT TEMPERATURES (K)

T(K)	Undecane		Hexadecane	
	Measured	Literature	Measured	Literature
303.	1.398	1.386	3.572	3.586
313.	1.198	1.204	2.932	2.957

(1) Viswanath and Natarajan (1989)

III. PREDICTIVE CAPABILITIES OF THE VISCOSITY MODELS

A. Application of Amin and Maddox model

As seen in the literature, Amin and Maddox (1980) proposed similar to equation (1) to model the kinematic viscosity of liquid petroleum fractions as a function of temperature by fitting the two parameters empirically. Parameters A and B in equation (1) related to the 50 % boiling point T_b , and the Watson characterization factor K , of each crude fraction and calculated as follows :-

$$\ln B = 4.717 + 0.00526T_b \quad (3)$$

$$A = 10^{-6}(91.836T_b^{-0.175} - 29.263)(K/B) \quad (4)$$

In this study, this model was used to predict the kinematic viscosities of investigated boiling temperature ranges. both parameters A and B are calculated from Eqs. (3) and (4) respectively. The results of testing the model for all the fractions show the overall AAD is 30.13 %..

B. Application of Lei et al. Model

Lei *et al.* (1999) proposed two-parameter viscosity equation for pure liquids on the basis of a modification of Eyring's absolute rate theory of liquid viscosity, the generalized equation of kinematic viscosity –temperature relationship is simply written as follows:

$$\ln(\nu/T) = 59.06(T_b)^{0.1546} M^{0.4791} \rho/T - (18.103 + \ln M) \quad (5)$$

Where the kinematic viscosity, ν is in m^2s^{-1} , T_b is 50 % boiling point, in $^\circ\text{C}$, and T is the temperature in K, ρ is the density in g/cm^3 , M is the molecular weight. In this correlation, ρ and M are estimated from the following equations respectively:

$$\rho = (\rho_{15.6}^2 - 1.1 \times 10^{-3} (T - 15.6))^{0.5} \quad (6)$$

$$M = 219.05 \exp(0.003924 (T_b + 273.15)) \exp(-3.075G) (T_b + 273.15)^{0.118} SG^{1.88} \quad (7)$$

As can be seen that, the coefficients in the viscosity equation are related to the characterization properties of petroleum fractions, which need only specific gravity at (60 $^\circ\text{F}$) and 50 % boiling point temperature as input parameters. Here, this model is tested using experimental viscosity data at

$$\ln \nu_m = \sum_{i=1}^n x_i^3 \ln(\nu_i M_i) + 3 \sum_{i=1}^n \sum_{\substack{j=1 \\ i \neq j}}^n x_i^2 x_j \ln(\nu_{ij} M_{ij}) + 6 \sum_{i=1}^n \sum_{\substack{j=1 \\ i < j}}^n \sum_{k=1}^n x_i x_j x_k \ln(\nu_{ijk} M_{ijk}) - \ln(M_{avg}) \quad (8)$$

Where ν_m is the kinematic viscosity of the mixture, x is the mole fraction of the component, M is the molecular weight.

As can be seen the McAllister model contains binary and ternary interaction parameters which are costly and time consuming for the determination therefore it significantly limits its reasonableness and usefulness (Asfour et al, 1991).

Nhaesi and Asfour (1998) developed a technique for the predicting of McAllister binary interaction parameters from pure-component properties for binary regular liquid mixtures.

In order to determine the numerical value of the effective carbon number, the following equation was reported (Nhaesi and Asfour, 1998):

$$\ln \nu = -1.943 + 0.193N \quad (9)$$

Where ν is the kinematic viscosity at (308.15 K), N is the effective carbon number.

IV. RESULTS AND DISCUSSION

In order to analyze and evaluate the performance of the considered viscosity models, the % absolute deviation (AD) and percent absolute average deviation (% AAD) are used and defined as follows:

$$\% AD = \frac{|\nu^{\text{exp}} - \nu^{\text{cal}}|}{\nu^{\text{exp}}} \times 100 \quad (10)$$

$$\% AAD = \frac{1}{n} \sum_{i=1}^n \frac{|\nu^{\text{exp}} - \nu^{\text{cal}}|}{\nu^{\text{exp}}} \times 100 \quad (11)$$

Where n is the number of experimental points, ν^{exp} the experimental viscosity and ν^{cal} the calculated viscosity. The %

several temperature levels. The overall % AAD is 9.78 %.

C. Application of McAllister model

McAllister (1960) developed a cubic equation for the kinematic viscosity of binary liquid mixtures based on Eyring's absolute rate theory. The results of the method were impressive; however, the method is correlative, as adjustable parameters have to be determined experimentally from viscosity-composition data.

Nhaesi and Asfour (2000) developed and reported a generalized form of the McAllister model suitable for multicomponent liquid systems. The reported model is given by

AAD indicates how close the calculated values are to experimental values.

A. Development of the McAllister model for undefined mixtures

The McAllister model is originally derived to deal with defined liquid mixtures. Nhaesi *et. al.*, (2001) Development of the model to treat the undefined fraction such as petroleum fuels. The following procedures have been carried out to predict the kinematic viscosity of petroleum fractions using McAllister model:

- Five Libyan Crude oils are fractionated into wide range of petroleum fractions in the boiling temperature ranges of (160-240 $^\circ\text{C}$) (160-280 $^\circ\text{C}$) and (240-340 $^\circ\text{C}$) then these fractions were distilled into an arbitrary number of sub-fractions.
- Each sub-fraction was considered to be a pure component (psoudocomponent).
- The molecular parameters for each sub-fraction was determined using the procedure outlined by American Petroleum Institute, API (1997) was followed for predicting the molecular parameters and pure component viscosities for each sub-fraction.
- The McAllister interaction parameters (binary and ternary) among the different sub-fraction were predicted based on method of Nhaesi and Asfour (2000).
- The effective carbon number Eq. (9) is determined using the kinematic viscosities of pure components at 308.15 K or based on API and mean average boiling point for each sub-fraction.
- The kinematic viscosities of pure components and the effective carbon numbers are used to yields the values of binary and ternary interaction parameters, respectively.
- The predicted parameters, along with the properties of the pure components are substituted into the appropriate form of

Equation (8) to obtain the kinematic viscosities of the undefined mixtures at a certain temperature

The % AD and % AAD for each fraction with different temperature considered herein is presented in *Table III*. It can be seen from the results that, the overall AAD is 3.39 % for these selected ranges.

TABLE III
COMPARISON OF PREDICTION ACCURACIES SEVERAL PETROLEUM FRACTIONS USING McALLISTER MODEL

Temp (K)	FR1	FR2	FR3	FR4	FR5
30	5.652	0.161	6.099	6.235	4.001
35	0.551	0.609	3.962	6.77	3.951
40	0.595	1.209	4.891	5.475	3.801
50	0.458	2.201	4.212	5.22	1.768
AAD%	1.814	1.045	4.791	5.925	3.38
Overall % AAD = 3.39 %					

Validation Of The Mcallister Model With Experimental Data

The accuracy and ability of McAllister model for predicting kinematic viscosity of petroleum fraction was checked with experimental data. Figure I depicts the comparison of experimental values of viscosity with predicted ones for Esidra kerosene fraction as an example. It is obvious from the figure that the model provides results in good agreement with experimental values.

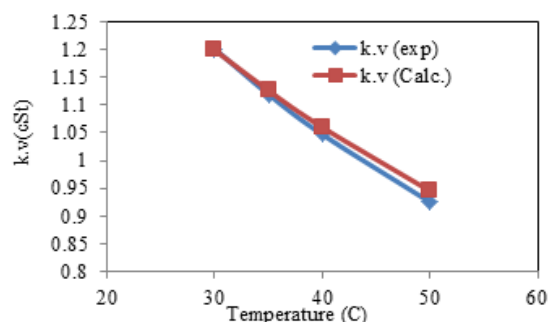


Fig. I Experimental kinematic viscosity values compared with calculated values (FR3)

B. Comparison between McAllister and the literature methods

The experimental data obtained in this study were used to test some of the viscosity models at various temperatures. Overall percentage AAD of the predictive capability of the model investigated in this study is summarized in Fig. II. The AAD bars in this Figure are placed in ascending order; the numbers above the bars are their values of AAD % error.

As can be seen from Fig. II, the value of the overall AAD resulting from the McAllister model is 3.39 %. Further there gave the lowest value of % AAD compared with literature models (Amin and Maddox; Li et al.) therefore this is more realistic than the other models.

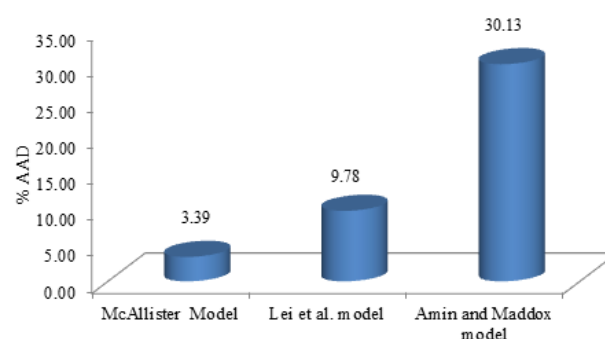


Fig. 2 Comparison of the predictive capabilities of the different predictive models.

V. CONCLUSION

The viscosity prediction using McAllister model has been tested against the experimental viscosity data of the fuels collected in our laboratory at several temperature levels (30, 35, 40, 50 °C). Good agreement between the predicted and experimental values have been observed. Furthermore, this model was compared with those predicted from the correlations of Lie et al., and Amin and Maddox models.

The viscosity predictions in the selected ranges at different temperature levels for the McAllister model appear to be much better than predictions made by other models with an overall average absolute deviation (%AAD) of 3.39 % compared with 9.78% and 30.13% for Lie et al. and Amin and Maddox models respectively. It can be seen that results indicated that the performance of our proposed technique is much better than the literature models.

Nomenclatures

A and B	Parameters in equation (1).
AAD	% average absolute deviation.
<i>i</i>	index number.
<i>j</i>	index number.
<i>k</i>	index number.
<i>M</i>	molecular weight, g/mol.
<i>N</i>	effective carbon number.
<i>C</i>	calibration constant of the viscometer (cSt/s).
<i>t</i>	measured flow time, s.
<i>T_b</i>	50 % boiling point temperature, °C.
<i>T</i>	temperature, K.
<i>SG</i>	specific gravity at (60 °F).
<i>x</i>	mole fraction
Greek Letters	
<i>ν</i>	Kinematic viscosity, m ² /s.
<i>η</i>	dynamic viscosity.
Superscripts	
avg	average.
cal	calculated viscosity value.
exp	experimental viscosity value.
Acronyms	
FRA	fraction

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