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Generalized equation predicts viscosity of heavy oil-solvent mixtures

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Abstract

Viscosity is one of the important physical properties required by engineers involved in pipeline shipment of heavy oil-solvent mixtures. The literature contains numerous correlations for predictions of viscosities of a variety of binary liquid mixtures. However, these equations are not suitable for heavy oil-solvent mixtures of large viscosity ratios. This paper presents two modified Puttagunta et al [13] viscosity correlations. The proposed new correlations have been verified using a viscosity data base of about 300 points, out of which 205 are new data. The data were obtained from binary mixtures made from five heavy oils and seven solvents, and from six lower molar mass hydrocarbon-solvent mixtures.

The modified correlations were used to predict viscosity-composition effects at constant temperature and viscosity-temperature effects at constant solvent composition. The overall average absolute deviations obtained were 3.8% for viscosity-composition effects and 1.3% for viscosity-temperature. We have expanded the applicability of the new correlation for viscosity-composition to include binary mixtures of simple hydrocarbon liquid, which predicted the viscosity of hexane-toluene mixtures with an average absolute deviation of 1.2% compared to 2.5% for the widely used additive equation. The correlations require viscosity as the only input parameter in order to make accurate predictions at any temperature or mixture composition.

1. Introduction

Heavy oils and bitumen are highly viscous and almost immobile at reservoir conditions. The commercial use of liquid diluents to reduce their viscosity in in-situ

production processes and in pipleline transportation have been well documented in literature [1-5]. Mitchell and Speight [5] showed that heavy oils have limited solubility in most hydrocarbon solvents and will precipitate asphaltene fractions beyond their threshold values.

Viscosity is one of the vital properties of crude oils and it is a critical parameter required in various aspects of petroleum engineering analysis. For simple binary mixtures the additive equation proposed by Arrhenius [6] is the most widely used method for predicting their viscosity. The equation given as:

$$\log \eta = X_A \log \eta_A + X_B \log \eta_B \tag{1}$$

is simple to use and fairly accurate for hydrocarbon mixtures whose components differ in viscosity by less than a factor of 100. X_A and X_B are mass fraction of component A and component B respectively. However, effort on the development of an accurate and generalized predictive equation for the viscosity of heavy oil-solvent mixtures has been met with limited success. Reid et al [7] and Miadonye and Puttagunta [8] have reviewed several of the correlations proposed by researchers.

Shu's [9] correlation for predicting the viscosity of a mixture is a modification of Lederer's equation and involved four equations:

$$\ln \eta = X_A \ln \eta_A + X_B \ln \eta_B \tag{2}$$

$$X_A = \frac{\alpha V_A}{\alpha V_A + V_B} \tag{3}$$

$$X_B = 1 - X_A \tag{4}$$

$$\alpha = 17.04(\Delta\rho^{0.5237})(\rho_A^{3.2745})(\rho_B^{1.6318}) \tag{5}$$

Other equations such as those proposed by Cragoe [10] and Chirinos et al [11] have been shown to predict mixtures viscosity within an average absolute error of 15 percent. However, the range of applicability of these correlations is limited, and for several of the correlations in literature values of physical properties are required experimentally which makes their application expensive, time consuming and cumbersome.

In this paper, two simple and generalized correlations previously developed by Miadonye et al [12] and Puttagunta et al [13] are modified for the predictions of new data for heavy oil-solvent mixtures. These correlations have been shown in several publications to have wider range of applicability, be more accurate and

simple-to-use than any correlation so far developed for the viscosity of bitumen-diluent mixtures. This study focused on two categories of heavy oil-solvent mixtures which are (1) the effect of increase in solvent mass fraction on viscosity at fix temperature, and (2) the viscosity-temperature relationship at fix solvent mass fraction.

For the first category, the general form of the Miadonye et al [12] equation given as follows was modified:

$$\nu_m = \exp\left\{\exp\left[a\left(1 - X_D^n\right)\right] + \ln \nu_D - 1\right\} \tag{6}$$

where a, is the viscosity interaction and n is the reduction parameter, It is derived as follows:

$$\alpha = \ln\left(\ln \nu_B - \ln \nu_D + 1\right) \tag{7}$$

$$n = \frac{\nu_D}{0.9184 * \nu_D + b_1} \tag{8}$$

The value of the parameter, b_1, obtained by non-linear regression analysis depends on the magnitude of the viscosity ratio between the pure components. One of the important characteristics of the correlation is that it requires no more than the knowledge of the pure heavy oil and the pure solvent viscosities to make viscosity predictions for the mixtures in all proportions.

The second category considered the fact that the viscosity variation with temperature for bitumen-solvent mixtures is characteristically similar to the viscosity-temperature relationships for pure bitumen, particularly for light petroleum crude. Thus, the viscosity-temperature correlation proposed by Puttagunta et al [13] was modified as follows:

$$\log_{10} \eta_M = \frac{b}{\left(1 + \dfrac{T - 37.78}{310.93}\right)^S} + C \tag{9}$$

The correlation has been shown to successfully predict the viscosity-temperature relationship of light petroleum crude based on a single viscosity measurement at 37.78°C. The viscosity characterization parameter, b, is obtained from the equation:

$$b = \log_{10} \eta_{37.78^oC} - C \tag{10}$$

The new values of the parameters, C, and S, were obtained by a non-linear regression technique as C = -1.6900 and S = 0.43306*b + 0.22696.

2. Experimental Details

The data used in this study were obtained partly from literature[12,14]. However, most of the data are new, obtained in our laboratory. The data consisted of a total number of 300 points obtained from binary mixtures of bitumen-solvent, heavy oil-solvent, paraffin-solvent and solvent-solvent in various proportions. The sources of the petroleum crude and solvents, and the literature data are summarized in Table 1.

The viscosity measurements conducted in our laboratory were done with a Cannon Fenske sizes 200 and 400 viscometers. The mixtures were made from paraffin-solvent, and UTF bitumen-naphtha. Briefly, large volumes of the binary mixtures for the required compositions were prepared and stoppered, and all measurements were made from these stocks. Solutions were prepared to an accuracy of 0.0004g/g using digital electronic balance. Viscosity measurements were carried out in accordance with ASTM -D445-61 for kinematic viscosity. The viscometers were vertically aligned by clamps in a water -filled bath equipped with a controlled heater. Solutions were temperature stabilized, and fluctuations of no more than $\pm$ 0.1^{o}C were observed. Four measurements of each viscosity with deviations of no more than 0.2% in efflux time were taken and averaged for each solution.

3. Results and Discussions

3.1 Correlation of solvent effects on viscosity of petroleum crude

Predictions with Equation (6) with different values of the viscosity reduction parameters were made for the viscosities of solvent-solvent mixtures and UTF bitumen-naphtha mixtures. The solvent-solvent mixtures (which were mixtures of hexane-toluene; hexane-benzene and hexane-ethylbenzene) as shown in Table 1 were correlated with both Equations (1) and (6). Both Equations are simple-to-use, and Equation (1) is widely used to estimate the viscosity of simple binary mixtures with good accuracy. The data were correlated with Equation (6) and the results compared with predictions made with Equation (1). The results summarized in Table 1 showed that the correlation Equation (6) predicted viscosity of the mixtures with greater accuracy than Equation (1). Figure 1 showed all the data to be either on or close to the diagonal line, representing a good match between experimental and predicted values. The overall average absolute deviation obtained was 1.2% compared to 2.6% for Equation (1).The result indicates that the equation can be successfully modified to model the viscosity of mixtures with a large viscosity ratios between the pure components.

Table 1. Summary of viscosity predictions made with Equations (1) and (6).

Temperature	Type of Binary Mixtures	Data Points	Average Absolute Deviations (%)	
			Equation (6)	*Equation (1)
	Solvent-Solvent System		b_1=.01291	
25°C	n-hexane + benzene	7	1.57	2.27
	+ toluene	9	0.976	2.09
	+ ethylbenzene	8	0.981	3.68
35°C	n-hexane + benzene	7	1.74	2.54
	+ toluene	9	0.980	1.85
	+ ethylbenzene	8	0.995	3.72
50°C	n-hexane + benzene	7	1.80	1.84
	+ toluene	9	0.955	1.77
	+ ethylbenzene	8	1.26	3.79
	overall ADD = 1.2%			=2.6%
	Heavy-oil Solvent System		b_1=.1291	
30°C	syncrude bitumen + condensate	6	3.80	
	Suncor bitumen + naphtha	6	3.83	
	heavy oil + naphtha	7	4.08	
	heavy oil + toluene	7	2.86	
60.3°C	Zuata crude + gasoil	12	4.43	
82.6°C	Zuata crude + gasoil	12	3.53	
	overall ADD = 3.8%			

**Equation (1) not suitable for mixtures with large viscosity ratio.*

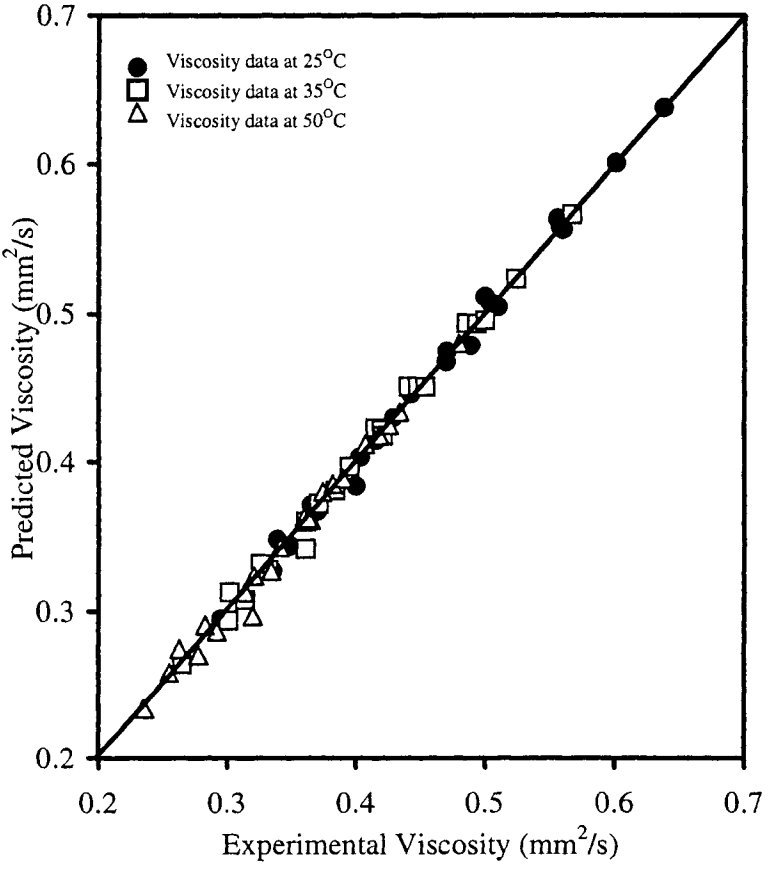

Figure 1: Comparison of Equation (6) predicted vs. experimental viscosities for simple binary mixtures at three temperatures.

To make predictions for the viscosity of heavy oil-solvent mixtures the new value for the parameter, b_1, as obtained by regression method was 0.1291. As shown in Table 1, the literature data was tested against the correlation Equation (6) with the new b_1, value. The predicted viscosity matched the measured viscosity very well with an overall average absolute deviation of 3.8%. Viscosity-solvent composition data were correlated at 30°C, 60.3°C and 80.2°C. As shown in Figure 2, the correlation gave good match between measured and predicted viscosities of the heavy oil-solvent mixtures at each temperature.

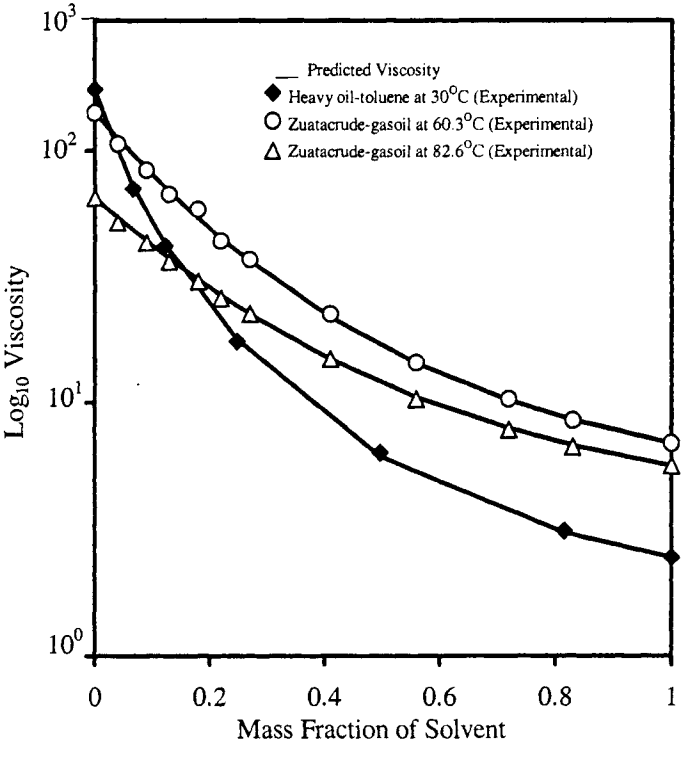

Figure 2: Viscosity-solvent mass fraction relationship for heavy oil-solvent mixtures predicted with Equation (6) at three fixed temperatures.

Typical examples of the prediction made for viscosities of solvent-solvent and heavy oil-solvent mixtures are depicted in Table 2. It should be noted that the correlation requires only the viscosities of the pure components in order to make predictions of the binary mixture viscosity at any solvent mass fraction.

Table 2. Comparison of viscosity values for typical predictions made with correlation Equations (1) and (6).

(a) n-hexane-toluene mixtures at 25°C with b_j=0.01291

Mass Percent Hexane	Measured Viscosity (mm^2/s)	Predicted Viscosity (mm^2/s)	Percent Error
0.00	0.558	0.558	0.00
12.1	0.504	0.511	-1.44
21.1	0.471	0.479	-1.70
29.9	0.443	0.450	-1.62
44.8	0.403	0.407	-1.00
60.0	0.370	0.370	0.13
71.2	0.349	0.345	1.01
100	0.295	0.295	0.00
Average Absolute Deviation = 0.98%			

(b) Toluene-Lloydminster heavy oil mixtures at 30°C with b_j = 0.1291

Mass Percent Toluene	Measured Viscosity (mm^2/s)	Predicted Viscosity (mm^2/s)	Percent Error
0.00	2967	2967	0.00
6.60	500.0	522.2	-4.43
12.3	173.0	178.8	-3.33
24.8	30.15	31.29	-3.79
49.7	4.050	3.812	5.89
81.5	0.991	0.965	2.64
100	0.614	0.614	0.00
Average Absolute Deviation = 2.9%			

3.2 Effect of temperature on viscosity of mixtures

Equation (9) was used to correlate the viscosity at different temperatures of two different binary mixtures of liquid hydrocarbons. The viscosity data, a total of 205 points, were obtained in our laboratory and have not been previously published. The data comprised of 129 data points from 18 binary mixtures of paraffin-solvent, and 18 data points from 3 binary mixtures of UTF bitumen-naphtha, measured at different temperatures. The correlation makes use of one single viscosity value of the mixture obtained at 37.78^{0}C to make predictions of viscosity at any temperature. For the new data correlated in this work, the correlation was modified to obtained new constant, C= -1.6900, and values for the parameter as S = .43306*b + .22696. The summary of the predictions made for the binary mixtures are given in Table 3.

Table 3. Summary of viscosity predictions made with Equation (9).

Type of Binary Mixture	Number of Mixtures	Total Data Points	Total AAD %
hexane-light paraffin	9	67	1.08
toluene- light paraffin	9	62	1.25
hexane-heavy paraffin	4	30	1.15
toluene-heavy paraffin	4	30	1.43
naphtha-UTF bitumen	3	16	1.15
Overall Average Absolute Deviation = 1.3%			

The results showed that mixtures made with hexane gave the most accurate viscosity estimations than mixtures made with toluene and naphtha. However, it is difficult to draw conclusions from these results as to the solubility characteristics of heavy petroleum in hexane. Figure 3 showed the comparison between predicted and measured viscosity at different temperatures and solvent mass fractions. It is evident from Figure 3 that for different mass fractions the correlation accurately predicts the effect of temperature on the mixtures viscosity. The overall prediction accuracy of the correlation is very good for each binary mixture type, with an overall average absolute deviation of 1.3% between measured and predicted viscosity.

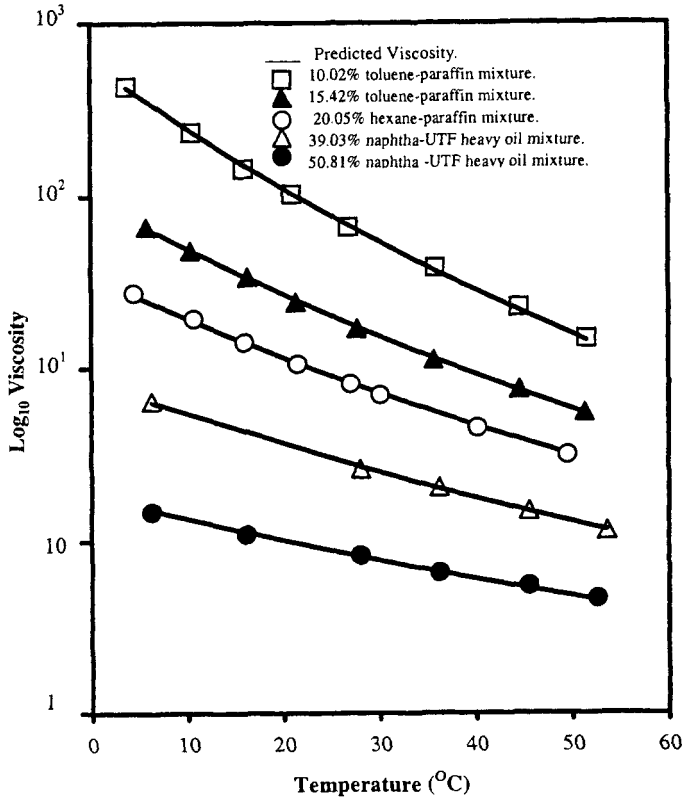

Figure 3: Viscosity-temperature relationship predicted with Equation (9) for various fixed compositions of petroleum-solvent binary mixtures.

Typical sample prediction made with the correlation Equation (9) is shown in Table 4 for naphtha-UTF bitumen. The only required input data for the correlation to predict viscosity of the mixture at any temperature is the mixture's viscosity at 37.78^{0}C.

Table 4. Typical viscosity predictions made with Equation (9).

Temperature (^{0}C)	Experimental Viscosity (mm^2/s)	Predicted Viscosity (mm^2/s)	% Error
(a) UTF-bitumen with 39.03% naphtha . $\eta_{37.780C}$=19.21 (mm^2/s)			
6.30	64.17	63.86	0.48
28.0	26.90	26.97	-0.27
36.2	20.42	20.25	0.82
45.5	14.94	14.96	-0.16
53.6	11.56	11.70	-1.2
			Average absolute deviation = 0.6%
(b) UTF-bitumen with 43.34% naphtha. $\eta_{37.780C}$ =15.95 (mm^2/s)			
16.2	32.97	33.70	-2.2
26.3	22.97	23.36	-1.7
36.2	17.08	16.78	1.8
45.5	12.70	12.58	0.94
52.6	10.45	10.24	2.0
			Average absolute deviation = 1.7%

4. Conclusion

The two viscosity correlations presented in this paper have been shown to accurately predict the viscosity of heavy oil-solvent mixtures. Correlation Equation (6) was used to predict the viscosity of heavy petroleum-solvent mixtures at a fixed temperature as the solvent composition increases. The overall absolute deviations obtained with this correlation for heavy petroleum-solvent mixtures was 3.8% and for solvent-solvent mixtures was 1.2%. The correlation required only the knowledge of viscosity of the pure components to make accurate predictions of their mixtures viscosity at any composition.

viscosity at any composition.

For the effect of temperature on viscosity of mixtures at fixed compositions, correlation Equation (9) was used. The correlation predicted the viscosity of each petroleum-solvent mixture at different temperatures with an overall average absolute deviation of 1.3% for a total number of 205 new data. The correlation, like Equation (6), is also simple to use and requires only one viscosity value of the binary mixture measured at 37.78^{0}C to make predictions at other temperatures.

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Nomenclature

b_1 regression constant in Equation 8

V_A volume fraction of component A

V_B volume fraction of component B

X_B mass fraction of heavy oil

X_D mass fraction of solvent

Greek Symbols

η_M viscosity of mixture

ν_B viscosity of heavy oil

ν_D viscosity of solvent

ν_M viscosity of mixture

ρ density of component

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