Generalized Method for Predicting Viscosities of Petroleum Fractions

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Introduction

According to a recent survey by Simulation Sciences Inc., a correlation for the prediction of liquid viscosities of petroleum fractions is highly desired. For petroleum fractions, useful viscosity prediction methods are most conveniently based on parameters such as boiling point and specific gravity, which are commonly used to characterize each fraction. Watson et al. (1935) presented figures relating kinematic viscosity as a function of American Petroleum Institute (API) gravity data and the Watson characterization factor K. These figures were obtained by plotting the data collected and drawing the best average curves by cross-interpolation. Recently, the API *Technical Data Book* (1978) replotted these two figures as a nomograph. From the values of API gravity and Watson characterization factor, one reads kinematic viscosity at 372.04 and 310.93 K.

The API *Technical Data Book* nomograph has proven useful over the years and is presently accepted as an industry-wide standard for estimating viscosities of light to moderately heavy oils. Abbott et al. (1970, 1971) have reduced the API nomograph to equations. In the comparison shown in Table 2, the Abbott correlations agree with the Watson plots quite well except at the high viscosity levels. Since the API nomograph is redrawn from the plots of Watson et al., the "data" read off the Watson plots are used in the comparison. While the correlations of Abbott et al. can be judged sufficiently representative of the API nomograph, they suffer from a serious shortcoming of singularity (Twu, 1985). This shortcoming reveals that the mathematical model of Abbott et al. is inadequate for significant extrapolations. Another evidence of the inadequacy of the model is that a different functional form is used at the two different temperatures. Due to this shortcoming, the correlations cannot be extrapolated smoothly into the regions where no experimental data are available. Smooth extrapolation is an important consideration in process simulation. Therefore, there is a need to develop a correlation to represent accurately the Watson plots, to be used in computer simulation. After a correlation representing Watson plots and the API nomograph is established, it can also be used as a basis for comparison with all other correlations developed thereafter.

The Two-Reference-Fluid Corresponding-States Method

Perturbation theory has been used widely in developing equations of state for predicting the thermodynamic properties of anisotropic fluids. Gubbins and Twu (1978) have successfully used the properties of a simple fluid as a reference and a suitable term for anisotropic forces to describe phase equilibria and other thermodynamic properties. The principle of the perturbation approach has also been employed semiempirically in the development of correlations for thermodynamic and transport properties (Twu, 1984; 1985). Pitzer (1955) and Pitzer et al. (1955) have demonstrated that for nonpolar fluids, the compressibility factor, Z, can be represented adequately by a linear function of the acentric factor ω:

$$Z = Z^{(o)} + Z^{(p)} \tag{1}$$

where $Z^{(o)}$ is the compressibility factor of a spherical molecular fluid and $Z^{(p)}$ represents the deviation of the compressibility factor of the real fluid from $Z^{(o)}$. $Z^{(o)}$ and $Z^{(p)}$ are functions of reduced temperature and reduced pressure. An alternative way of writing Eq. 1 is given by Lee and Kesler (1975), who use two reference systems instead of only one reference, and express the compressibility factor of any fluid in terms of the compressibility factor of a simple fluid, $Z^{(o)}$, and the compressibility factor of a reference fluid, $Z^{(r)}$, as follows:

$$Z = Z^{(o)} + \frac{\omega}{\omega^{(r)}}[Z^{(r)} - Z^{(o)}] \tag{2}$$

Both $Z^{(o)}$ and $Z^{(r)}$ are given by the same form. The Lee-Kesler correlation provides an analytical framework for the three-parameter corresponding-states principle.

More recently, Teja (1980) has shown that Eq. 2 can be extended further so that the simple fluid is no longer retained as one of the references. Equation 2 is written as:

$$Z = Z^{(r1)} + \frac{\omega - \omega^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}} [Z^{(r2)} - Z^{(r1)}] \tag{3}$$

where the superscripts ($r1$) and ($r2$) refer to two reference fluids. If one of the reference fluids is a simple fluid of zero acentric factor, then Eq. 3 reduces to Eq. 2.

Watson plots show that the logarithmic function of viscosity at the same boiling point temperature is a linear function of API gravity. Therefore, in an analogous manner, Eq. 3 is extended to viscosities in this work as follows:

$$\ln(\nu) = \ln(\nu^{(r1)}) + \frac{\mathrm{API} - \mathrm{API}^{(r1)}}{\mathrm{API}^{(r2)} - \mathrm{API}^{(r1)}} [\ln(\nu^{(r2)}) - \ln(\nu^{(r1)})] \tag{4}$$

where ν is kinematic viscosity of the petroleum fraction in cSt ($= 10^{-6} \mathrm{m}^2/\mathrm{s}$) at either 372.04 or 310.93 K. ν, $\nu^{(r1)}$ and $\nu^{(r2)}$ are evaluated at the same boiling point. The superscripts ($r1$) and ($r2$) again refer to two reference fluids. API is the API gravity, which has the relationship with specific gravity, SG: API = 141.5/SG − 131.5.

Since all the calculations are made at the same boiling point, Eq. 4 can be simplified based on the definitions of Watson characterization factor and of API gravity as:

$$\nu = \nu^{(r1)} \left[\frac{\nu^{(r2)}}{\nu^{(r1)}}\right]^{(1/2)(K-10)} \tag{5}$$

where K is the Watson characterization factor.

Correlation of the Reference Fluid

The viscosity of the reference fluid can be obtained from the plots of Watson et al. (1935). These data have been correlated as a function of the boiling point temperature of petroleum fraction by means of the following equation:

$$\ln(\nu^{(r)}) = C_1 + \frac{C_2}{T_b} + C_3 \ln(T_b) + C_4 T_b + C_5 T_b^3 + C_6 T_b^6 \tag{6}$$

where C_1 to C_6 are constants to be fitted. T_b is the boiling point temperature of the petroleum fraction in degrees Rankine. $\nu^{(r)}$ is the reference viscosity in cSt at either 372.04 or 310.93 K.

To choose the reference equation, the capability of extrapolation to a high boiling point by the equation itself is the primary consideration. Equation 6 not only gives accurate representation of the viscosity, but extrapolates smoothly to very high boiling points, higher than the correlation of Watson et al. The choice of reference viscosities is also carefully considered. The accuracy of any corresponding states theory depends on the choice of the reference system. The closer the system of interest is to the reference system, the more accurate the theory will be. For this reason, petroleum fractions with the same boiling point as the system of interest are chosen as the reference systems. In this work, two hypothetical petroleum fractions with Watson K equal to 10 and 12 are chosen as reference fluids.

The purpose of this paper is to reproduce the Watson plots by an analytical equation. Therefore, all the "data" used in regression to derive constants in Eq. 6 are read from Watson plots. These are smoothed values and are not actual experimental data. In this work, the viscosity data are taken from the Watson plots for Watson K equal to 10 and 12. Each viscosity data point with given Watson K is associated with an API gravity. From the given Watson K and API gravity, the boiling point temperature of the viscosity for a petroleum fraction can be obtained. According to the Watson plots, the viscosity of the petroleum fractions either at 372.04 or 310.93 K is only a function of boiling point temperature at a given Watson K.

With the data taken from the Watson plots, the constants C_1 to C_6 in Eq. 6 can easily be obtained by least-squares regression. All coefficients are statistically significant. After deriving these constants, Eq. 6 is plotted over a wide range as a function of boiling point temperature to ensure that all curves are smooth with no irregularity. Table 1 lists these constants for Watson K equal to 10 and 12 at 372.04 and 310.93 K. It is interesting to note that the constants for 372.04 K are generally of the same magnitude and sign as those for 310.93 K. Should the experimental viscosities of any petroleum fraction not be available, then Eq. 5 and the viscosities of two reference fluids can easily be used to predict the unknown viscosity of the petroleum fraction.

Calculational Procedure

The calculation of the viscosity of any petroleum fraction at a given boiling point temperature T_b and specific gravity SG may be carried out as follows. First one evaluates $\nu^{(r1)}$, $\nu^{(r2)}$ and K in Eq. 5. The properties of references are evaluated at the same boiling point temperature as the system of interest. $\nu^{(r1)}$ and $\nu^{(r2)}$ at 372.04 K can be calculated by substituting T_b into Eq. 6 with the appropriate constants for $K = 10$ and $K = 12$. These constants are listed in Table 1. The Watson K factor can be calculated from the given boiling point temperature T_b and specific gravity SG using the equation $K = T_b^{1/3}/\mathrm{SG}$.

Since all these quantities are now known, the viscosity at 372.04 K of the petroleum fraction at given T_b and SG can be readily calculated from Eq. 5. This procedure is repeated for calculating viscosity at 310.9 K by replacing $\nu^{(r1)}$ and $\nu^{(r2)}$ at 372.04 K with those at 310.93 K. The viscosity at any desired temperature can be calculated from viscosity data at two known temperature points. The details of calculating viscosity at other temperatures has been described by Twu (1985). The calculations require no iterations, so that the whole procedure may be easily carried out on a calculator.

Results and Discussion

Table 1. Constants to be Used in Eq. 6

K	Constant	372.04 K	310.93 K
10	C_1	−258.131	−234.362
	C_2	11,124.9	7,831.91
	C_3	40.4918	38.3044
	C_4	−0.0356499	−0.0430100
	C_5	0.281192×10^{-8}	0.555144×10^{-8}
	C_6	0.468001×10^{-18}	0.841988×10^{-18}
12	C_1	−243.268	−509.138
	C_2	11,787.9	22,615.7
	C_3	37.3558	80.4388
	C_4	−0.0283454	−0.0763095
	C_5	0.162873×10^{-8}	0.819108×10^{-8}
	C_6	0.406341×10^{-18}	0.244956×10^{-18}

Table 2 gives a comparison of the Watson plots (1935), the correlations of Abbott et al. (1970, 1971), and this work for the

Table 2. Comparison of Viscosities

K	API	Viscosity at 372.04K, cSt					Viscosity at 310.93K, cSt				
		Watson et al.	Abbott et al.		This Work		Watson et al.	Abbott et al.		This Work	
			Calc.	Dev. %	Calc.	Dev. %		Calc.	Dev. %	Calc.	Dev. %
10.0	0	8.8	8.48	−3.64	8.85	0.57	185.0	198.0	7.03	189.0	2.16
	5	2.7	2.82	4.44	2.72	0.74	16.0	17.5	9.38	16.0	0.00
	10	1.4	1.49	6.43	1.39	−0.71	4.3	4.76	10.70	4.27	−0.70
	15	0.91	0.98	7.69	0.90	−1.10	2.0	2.11	5.50	2.00	0.00
	20	0.63	0.73	15.87	0.64	1.59	1.2	1.21	0.83	1.23	2.50
10.5	5	13.6	12.4	−8.82	13.3	−2.21	390.0	361.0	−7.44	392.0	0.51
	10	3.7	3.63	−1.89	3.60	−2.70	30.0	26.2	−12.67	26.8	−10.67
	15	1.7	1.79	5.29	1.70	0.00	6.5	6.46	−0.62	6.12	−5.85
	20	1.06	1.14	7.55	1.05	−0.94	2.6	2.70	3.85	2.59	−0.38
	25	0.75	0.82	9.33	0.74	−1.33	1.5	1.49	−0.67	1.50	0.00
	30	0.55	0.65	18.18	0.55	0.00	0.99	0.97	−2.02	1.00	1.01
11.0	10	20.7	18.4	−11.11	19.9	−3.86	760.0	670.0	−11.84	739.0	−2.76
	15	4.9	4.72	−3.67	4.76	−2.86	44.0	39.7	−9.77	43.8	−0.45
	20	2.1	2.18	3.81	2.10	0.00	9.3	8.85	−4.84	8.81	−5.27
	25	1.23	1.33	8.13	1.24	0.81	3.4	3.48	2.35	3.39	−0.29
	30	0.85	0.94	10.59	0.85	0.00	1.8	1.85	2.78	1.84	2.22
	35	0.63	0.73	15.87	0.63	0.00	1.2	1.16	−3.33	1.19	−0.83
11.5	15	31.0	27.9	−10.00	29.2	−5.81	*	1,271.0	*	1,218.0	*
	20	6.3	6.20	−1.59	6.27	−0.48	66.0	61.0	−7.58	67.7	2.58
	25	2.6	2.67	2.69	2.58	−0.77	13.0	12.2	−6.15	12.5	−3.85
	30	1.46	1.55	6.16	1.47	0.68	4.4	4.51	2.50	4.45	1.14
	35	0.99	1.07	8.08	0.98	−1.01	2.3	2.29	−0.43	2.28	−0.87
	40	0.72	0.81	12.50	0.71	−1.39	1.4	1.40	0.00	1.42	1.43
12.0	25	8.2	8.24	0.49	8.17	−0.37	97.0	94.8	−2.27	96.4	−0.62
	30	3.2	3.28	2.50	3.16	−1.25	17.0	17.0	0.00	17.1	0.59
	35	1.7	1.83	7.65	1.73	1.76	5.7	5.89	3.33	5.80	1.75
	40	1.1	1.22	10.91	1.13	2.73	2.8	2.86	2.14	2.84	1.43
	45	0.81	0.91	12.35	0.81	0.00	1.7	1.70	0.00	1.71	0.59
12.5	25	57.0	69.5	21.93	57.4	0.70	*	4,901.0	*	1,855.0	*
	30	10.0	11.1	11.00	10.5	5.00	105.0	149.0	41.90	122.0	16.19
	35	3.7	4.06	9.73	3.84	3.78	22.0	23.9	8.64	22.2	0.91
	40	2.0	2.16	8.00	2.03	1.50	7.1	7.73	8.87	7.37	3.80
	45	1.3	1.40	7.69	1.30	0.00	3.2	3.60	12.50	3.50	9.38
	50	0.92	1.02	10.87	0.92	0.00	2.0	2.07	3.50	2.05	2.50
	55	0.68	0.80	17.65	0.69	1.47	1.3	1.36	4.62	1.35	3.85
AAD%	—	—	—	8.69	—	1.37	—	—	6.06	—	2.64

* = not applicable
AAD % = average absolute deviation percent
SI conversion: cSt = 10^{-6} m^2/s

calculation of kinematic viscosity over the valid range of the API nomograph. Point-by-point comparisons of the correlation in this work with the Watson plots show agreement practically within graph-reading error except for two points at 310.93 K. One is at $K = 10.5$ and API = 10. The other is at $K = 12.5$ and API = 30. The discrepancy of these two points, however, may be due to the internal inconsistency of the Watson plots. During the comparison, the shortcomings of the Abbott correlations become evident while making a small extrapolation. For example, one calculated value from the Abbott correlations at $K = 12.5$ and API = 25 at 310.93 K gives a large number. Further extrapolation shows that the Abbott correlations are approaching a region of singularity.

In conclusion, the Watson plots or API *Technical Data Book* viscosity nomograph can be generated by using a corresponding-states principle based on the viscosities of two reference fluids. With a suitable choice of reference fluids and of the reference equation, the Watson plots can not only be represented accurately by a simple analytic equation, but significantly extended to a wider range of applicability. The conversion of charts to an analytic equation is believed to be useful in engineering problems when process simulation is required.

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Notation

API gravity = 141.5/SG − 131.5
$C_1, \ldots, C_6$ = constants in the viscosity reference equation, Eq. 6
K = Watson characterization factor = $T_b^{(1/3)}$/SG
ln = logarithmic function, base e
SG = specific gravity at 288.71 K
T_b = normal boiling point temperature, °R (K = °R/1.8)
Z = compressibility factor
ν = kinematic viscosity, cSt (cSt = 10^{-6}m^2/s)
ω = acentric factor

Superscripts

o = spherical reference fluid
p = perturbation part
r = reference fluid
$r1, r2$ = reference fluids $r1, r2$

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