Correlations for Viscosity of Kraft Black Liquors at Low Solids Concentrations

Abbas A. Zaman and Arthur L. Fricke
Dept. of Chemical Engineering, University of Florida, Gainesville, FL 32611

The kinematic viscosities of several kraft black liquors from a two-level, four-variables, factorial-designed experiments for pulping slash pine were determined for solids concentrations from 10 to 50% and temperatures up to 80°C by glass capillary methods. The four pulping variables were cooking time, cooking temperature, sulfidity, and effective alkali. Relationships between temperature and kinematic viscosity have been developed by using free volume and absolute rate theories. The results from these two methods have been compared and discussed. A reduced variables method for dilute polymer solutions was used to correlate the viscosity with the combined effect of temperature and solids concentration.

The viscosity of black liquor is an important parameter in the design and performance of kraft recovery systems. The energy efficiency will be increased by firing black liquors at higher solids concentrations (Fricke, 1987). To evaporate the liquor most efficiently and to achieve higher concentrations, knowledge of viscosity over a wide range of temperatures and solids concentrations is essential. The purpose of this study is to evaluate the utility of various fundamentally based models for correlating viscosity data of black liquors as a function of temperature and concentration of nonvolatile components in the region in which the liquors behave as Newtonian fluids.

Background

Several viscosity data for black liquors have been reported, but relatively few studies have been performed on the viscosity-temperature and viscosity-concentration relations: Morre (1923), Kobe and McCormack (1949), Hunter et al. (1953), Harvin (1955), Han (1957), Melcher (1961), Bodenheimer (1969), Polyakov et al. (1970), Wight (1985), and Fricke (1985, 1987) have reported viscosity data for black liquors for solids contents below 50% and for temperatures up to 100°C.

Wight (1985) and Fricke (1985, 1987) have shown that black liquors behave as Newtonian fluids at concentrations up to 50%. Small (1984) has shown that lignin degradation does not occur in liquors at solids concentrations below 50% and temperatures below 100°C at times up to several days; therefore, at these conditions, the viscosity can be determined by using glass capillary methods.

Extensive work on black liquor composition has been done by Fricke (1985, 1987, 1990) and other investigators (Rydholm, 1965). They reported that black liquor at low solids concentrations is a complex solution of organic and inorganic components in water. The nonvolatile constituents consist of lignin, low-molecular-weight organic components, and inorganic salts dissolved in water during the pulping process. It is widely known that the lignin concentration and its molecular weight, organic-to-inorganic ratio, and inorganic component concentrations in nonvolatiles are affected by the pulping conditions (Fricke, 1987, 1990). Lignin is a polymer that composes up to 50% of the organic components (Small, 1984, 1985; Wight, 1985; Fricke, 1985, 1987) and has an important effect on the viscosity. Therefore, black liquor can be expected to behave as a polymer solution, and theories developed for polymer solutions should be useful for modeling the viscosity data.

Although the viscosity of black liquor is affected mainly by the lignin concentration and molecular weight, it is also affected by inorganics concentration (Fricke, 1987).

Viscosity-Temperature Relationships

Two different approaches have been used to derive expressions for the temperature dependence of viscosity. One is associated with the theory of absolute reaction rates and the other with the free volume theory. Because of two different mechanisms, the final expressions for the temperature dependence of viscosity differ in these approaches.

Probably, the most successful theories of liquid viscosity have been based on the assumption of a quasicrystalline liquid structure (Macedo and Litovitz, 1965). A molecule is considered to vibrate about an equilibrium position, and transition from this state is possible when it possesses sufficient energy, and a free space is available into which the molecule can jump to attain a new equilibrium position.

If the probability of accumulation of the energy required to overcome the potential energy barrier is P_E and the probability of free volume existing near the initial equilibrium position is P_v, then the total probability of a transition or jump from one site to another is (Macedo and Litovitz, 1965):

Correspondence concerning this work should be addressed to A. L. Fricke.

$$P=P_E\times P_v \quad (1)$$

Eyring (1935, 1936, 1937) developed the theory of absolute reaction rates and made extensive use of the concepts of free volume in the flow of liquids. Instead of using P as in Eq. 1, however, to express the total probability of a transition, he used P_E; therefore, the temperature dependence of viscosity reduces to determining the number of possible jumps of molecular units over the potential barrier at different temperatures in his approach.

Application of the general methods of absolute rate theory, with the assumption that the molar volume and entropy are independent of temperature, leads to the following relationship for the viscosity of liquids (Vinogradov and Malkin, 1980):

$$\eta=A\ \exp\left(\frac{E}{RT}\right) \quad (2)$$

where A is a constant and E is the activation energy for flow. Equation 2 has been derived empirically by De Gusman (1913) and other investigators (such as Arrhenius, 1916). It was derived theoretically by Andrade (1930) and other workers (such as Frenkel, 1925). Equation 2 is usually successful for simple nonassociated liquids, but fails to account for the temperature dependence of the viscosity of associated liquids and polymeric liquids (Macedo Litovitz, 1965). For this reason, the free volume approach has been considered by many investigators for liquids and polymer solutions. The free volume theory is based on the observations by Doolittle (1951), who studied the viscosity of n-alkanes. Doolittle and Ferry et al. (1955) have shown that the dependence of viscosity on free volume can be expressed as:

$$\eta=A\ \exp\left(\frac{BV_o}{V_f}\right) \quad (3)$$

where

A, B = constants
V_o = specific volume occupied by the molecules of the substance
V_f = $(V-V_o)$ = free volume
V = specific volume of the liquid

Cohen and Turnbull (1959, 1961, 1970) showed that Eq. 3 can be derived by associating a local free volume with each molecule and assuming a distribution of local free volumes. They considered a liquid consisting of hard spheres and repulsive forces only.

Many workers (including Macedo and Litovitz, 1965), have reported that Eqs. 2 and 3 fail to account for the temperature dependence of the shear viscosity of many liquids when they are over 373.2 K above the glass transition temperature and also below it. Also, these equations predict that

$$\left(\frac{\partial(\log_e\eta)}{\partial(T)}\right)_v=0,$$

which is not true for most of the liquids. Barlow et al. (1965), Matheson (1966), Miller (1963), Van Velzen et al. (1972), Chhabra and Hunter (1981), Przezdziecki and Sridhar (1985), and Luckas and Lucas (1986) have modified these equations in various ways to increase the region of validity. Barlow considered the effect of temperature on density, and Matheson has taken into account the pressure dependence of free volume.

Macedo and Litovitz (1965), by reconsidering the Eyring rate and free volume theories and combining these two effects with the assumption that the free volume is the total thermal expansion at constant pressure have proposed the following equation:

$$\eta=A\ \exp\left\{\frac{E_v}{RT}+\frac{\alpha T_o}{T-T_o}\right\} \quad (4)$$

where E_v is the activation energy for flow at constant volume, T_o is the apparent temperature where the free volume becomes zero, and α is a constant.

Dienes (1953) also considered a temperature-dependent activation energy for non-Arrhenius behavior of the viscosity and obtained an equation which is similar to Eq. 4.

The coefficient A in Eqs. 2 and 3 is temperature-dependent, and various investigators (such as Gubbins and Tham, 1969) have predicted that A varies with $T^{1/2}$. Such a temperature dependence is assumed in this work. Equation 4 will reduce to Eq. 2 if the liquid has a very small thermal expansion coefficient and if V_f is independent of temperature. It will reduce to Eq. 3 if the activation energy for flow is negligible.

Figures 1 through 3 are representatives of log μ (kinematic viscosity) vs. $1/T$ for some of the liquors at solid concentrations below 50%. At lower solids contents, the plots are close to being straight lines, but the nonlinear behavior is more significant at higher concentrations. The effect of free volume on viscosity probably becomes more important at higher concentrations. To obtain the best correlations for viscosity as a function of temperature for different black liquors at low solids concentrations and to find the best model for extrapolation at higher temperatures at a fixed concentration, both free volume and absolute rate theories have been examined in this work, and the results have been compared. Equations 2 and 3 can be written as:

$$\eta=A_1T^{1/2}\ \exp\left[\frac{B_1}{T}\right] \quad (5)$$

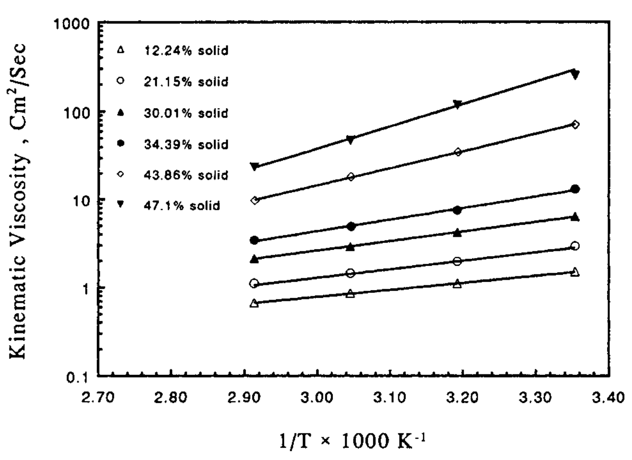

Figure 1. Kinematic viscosity as a function of temperature for black liquor ABAFX015,16.

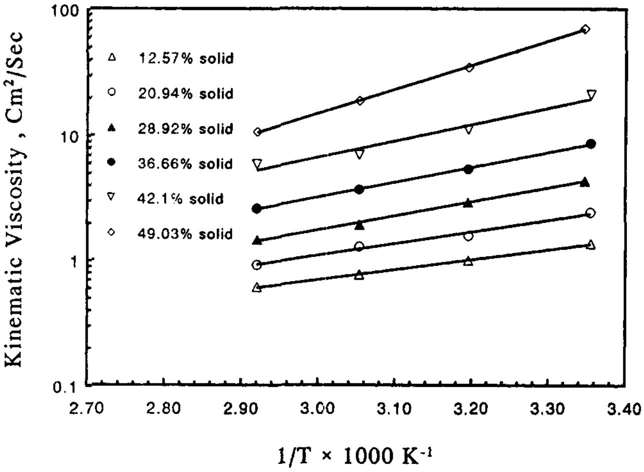

Figure 2. Kinematic viscosity as a function of temperature for black liquor ABAFX025,26.

$$\eta = A_2 T^{1/2} \exp\left(\frac{B_2 T_o}{T - T_o}\right) \qquad (6)$$

where

A_1, A_2, B_1, B_2 = constants

T_o = temperature where free volume equals zero

Masse (1984) has studied the phase diagram for three black liquors. His results show that the freezing point of black liquors ($\leq 50\%$) is a strong function of solids concentrations and varies from 273.2 K to 183 K.

Table 1. Pulping Conditions and Kappa Numbers for Black Liquors.

Black Liquor	Cooking Time h	Temp. K	Effective Alkali %	Sulfidity %	Kappa No.
ABAFX015,16	1.333	438.7	16	20	61.1
ABAFX025,26	1.333	450.0	16	35	18.5
ABAFX035,36	0.667	438.7	13	35	77.0
ABAFX043,44	1.000	444.4	14.5	27.5	51.1
ABAFX053,54	1.000	444.4	11.5	27.5	42.0

In this work, Eqs. 5 and 6 have been used to fit the experimental data for viscosity of 23 different kraft black liquors from laboratory cooks of slash pine. The cooks were done at a liquor-to-wood ratio of 4/1. Details of pulping, experimental procedure and pertinent details for digesters are given by Zaman et al. (1991). The cooking conditions and Kappa numbers for some of the liquors are summarized in Table 1. At first, we chose the approximate values for T_o in Eq. 6 as a function of concentration for each liquor by considering Masse's work, and then we tried to choose an average value for T_o over the whole range of solids concentrations (close to $T_o = 220$ K). The difference between the results are insignificant. A fixed value of $T_o = 220$ K for all liquors will give very good results with $R^2 \geq 0.99$ for all liquors at different solids concentrations. R^2 for Eq. 5 is also greater than 0.99. At lower concentrations, the results using Eq. 5 are better than Eq. 6 (smaller errors), but it seems that, above 40% solids, both theories yield equally accurate correlations. Coefficients A_1, B_1, A_2, and B_2 are summarized in Tables 2 and 3 for one of the liquors. As can be observed, the constants for this liquor are concentration-dependent, and attempts were made to determine consistent relationships for constants as a function of concentration. The results will be discussed later.

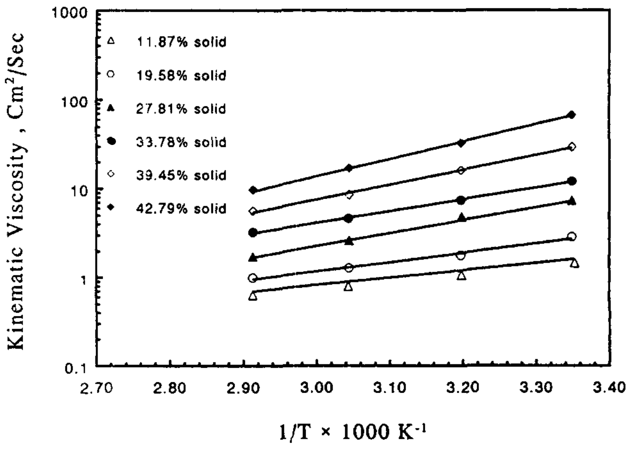

Figure 3. Kinematic viscosity as a function of temperature for black liquor ABAFX043,44.

Reduced Correlation for Low Solids Viscosity

The concepts of reduced variables methods for dilute polymer solutions as suggested by several investigators (Ferry, 1980; Billmeyer, 1971; Vinogradov, 1980) can be used to reduce the viscosity data for black liquors at low solids concentration as reported earlier (Fricke, 1985, 1987; Wight, 1985; Adams, 1988).

Using the relative kinematic viscosity with respect to water (the solvent), $\mu_R = (\mu/\mu_w)$, and defining the combined concentration-temperature variable as:

$$X = \frac{S}{T} \qquad (7)$$

where

S = solids mass fraction

T = absolute temperature

on the assumption that the lignin polymer concentration is

Table 2. Coefficients of Eq. 5 for Black Liquor ABAFX015,16

% Solids	A_1	B_1	R^2
12.24	1.12×10^{-4}	1,985.41	1
21.15	5.55×10^{-5}	2,383.47	0.997
30.01	4.87×10^{-5}	2,664.64	1
34.39	1.59×10^{-5}	3,206.03	0.997
43.86	6.22×10^{-7}	4,689.54	1
47.10	4.14×10^{-8}	5,915.7	0.998

Table 3. Coefficients of Eq. 6 for Black Liquor ABAFX015,16

% Solids	A_2	B_2	R^2
12.24	8.42×10^{-3}	0.8424	0.992
21.15	1.0×10^{-2}	1.016	0.996
30.01	1.58×10^{-2}	1.132	0.994
34.39	1.66×10^{-2}	1.367	0.999
43.86	1.67×10^{-2}	1.985	0.99
47.10	7.7×10^{-3}	2.87	1

proportional to the solids concentration, one can express the reduced viscosity as:

$$\log_e(\mu_R)=\sum_{i=1}^{n} a_i\left(\frac{S}{T}\right)^i \tag{8}$$

Figure 4 represents the reduced form of the data for different black liquors. A polynomial of degree 2 will fit the experimental data with $R^2\geq0.997$. The constants a_1, a_2 and R^2 have been summarized in Table 4 for some of the liquors.

Table 4. Coefficients of Eq. 8 for Black Liquors

Black Liquor	$a_1\times10^{-2}$	$a_2\times10^{-4}$	R^2
ABAFX015,16	4.76	168.04	0.998
ABAFX025,26	3.51	135.78	0.999
ABAFX035,36	5.30	144.44	0.998
ABAFX043,44	6.10	160.00	0.999
ABAFX053,54	5.23	174.73	0.999

Results and Discussion

The model based on the absolute rate theory (Eq. 5) is a two-constant model, A_1 and B_1, with B_1 related to the activation energy for flow. Equation 6 which is based on free volume theory is a three-constant model, but one constant (T_o) can be a set value for all liquors. These give results of high accuracy and can be used for extrapolation of temperature effect on viscosity at a fixed concentration. The corresponding states model (Eq. 8) is not quite as good for extrapolation to high temperatures at a fixed concentration; however, it includes the effect of concentration. Equation 5 could not be used to give A_1 and B_1 as correlatable functions of concentration. Since the constants in the equation are not universal, these must be evaluated for each liquor and thus have no predictive value. Equation 6 could be arranged such that:

$$A_2=f(\text{concentration})=A_2'+A_2''S \tag{9}$$

for all liquors of one species. For the liquors used in this study, A_2 will be equal to:

$$A_2=2.75\times10^{-3}+3.18\times10^{-4}S \tag{10}$$

The value of A_2 can be replaced in Eq. 6, and the values of B_2 can be recalculated for each liquor at different solids concentration. The new values of B_2 and R^2 for one liquor have been summarized in Table 5. With this approach, the accuracy of the fits will be increased since $R^2\simeq1$ for all liquors. Figure 5 represents B_2 as a function of solids concentration for each liquor. As can be observed, B_2 for a single liquor may be written as:

$$B_2=B_2'+B_2''S+B_2'''S^2 \tag{11}$$

The values of B_2', B_2'', and B_2''' can be calculated for each liquor and replaced in Eq. 6 which then can be used to calculate the viscosity of the corresponding liquor at any temperature or concentration. In this approach, however, the final model for viscosity involves five constants in addition to T_o, and B_2', B_2'', and B_2''' are functions of solids composition. The accuracy of this model is higher than the corresponding states model involving two constants, a_1 and a_2, which are functions of solids composition.

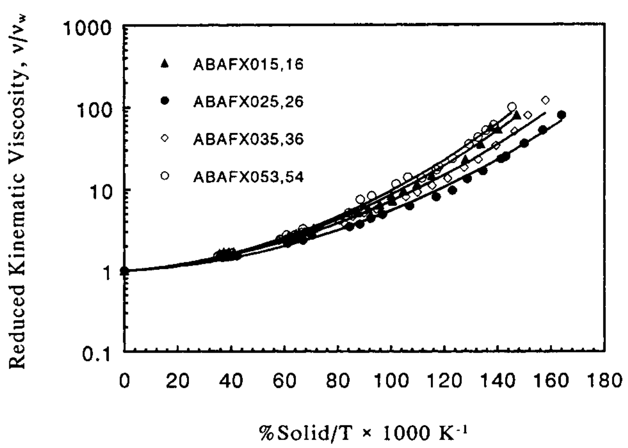

Figure 4. Reduced kinematic viscosity for different black liquors.

Conclusions

At low solids ($\leq50\%$), black liquor can be treated as a polymer solution and the theories developed for dilute polymer solutions can be used to correlate viscosity data with temperature and solids concentrations. The relationship between viscosity and temperature can be expressed by using either free

Table 5. B_2 as in Eq. 6 for Black Liquor ABAFX015,16 with A_2 Considered as a Universal Constant

% Solids	B_2	R^2
12.24	0.9454	0.9995
21.15	1.04	1.0
30.01	1.2416	0.9996
34.39	1.4506	1.0
43.86	1.986	0.9997
47.10	2.4685	1

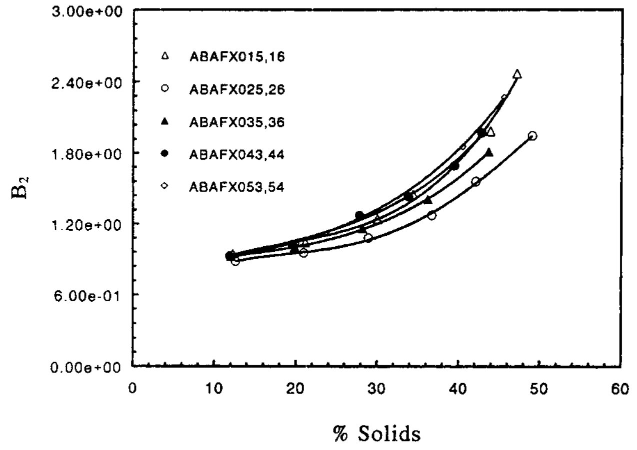

Figure 5. B_2 as a function of solids concentration for different black liquors.

volume theory and an average value for freezing point of the liquors or absolute rate theory. The constant A_2 in Eq. 6, however, can be universal for all liquors of one species, and the constant B_2, which depends on the solids composition, can be written as a function of solids concentrations for a single liquor. Therefore, a model based on free volume theory is probably the best for 1) defining the viscosity of a liquor as a function of temperature and solids contents and 2) extrapolation to higher temperatures at a fixed concentration. The corresponding states can be used to correlate the relative viscosity with respect to water (solvent) as a function of S/T as the correlating variable. This is less time-consuming and easier to use, but one cannot expect to have higher precision than Eq. 6. The constants a_1 and a_2 will be correlated empirically with nonvolatiles composition and pulping conditions for single species in future work. In general, the viscosity is not only affected by temperature and solids concentration of the liquors, but is also a function of cooking conditions that lead to variations in solids composition and lignin molecular weight. However, more statistical work has to be performed to determine the effects of cooking time, cooking temperature, effective alkali, and sulfidity on the viscosity of black liquor.

Acknowledgment

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Errata

- In the article titled "Nucleation Mechanisms and Particle Size Distributions of Polymer Colloids" (July 1993, p. 1210), Eq. 1 on p. 1212 should read as:

$$\frac{\partial \mathbf{n}(v,\, t)}{\partial t} = \mathbf{\Omega n}(v,\, t) - \frac{\partial}{\partial v}[\mathbf{Kn}(v,\, t)] + \mathbf{c}(v,\, t) \quad (1)$$

- In the note titled "An Infinite Series Solution for the Creeping Radial Entrance Flow of a Newtonian Fluid" (September 1993, p. 1563), Eq. 13 on p. 1564 should read as:

$$C(\beta) = \frac{\kappa\beta A(\beta)[\kappa\beta + \sinh\kappa\beta\cosh\kappa\beta]}{\sinh^2\kappa\beta - \kappa^2\beta^2} + \frac{\kappa\beta E(\beta)\sinh^2\kappa\beta}{\sinh^2\kappa\beta - \kappa^2\beta^2} \quad (13)$$