Athabasca Bitumen: Oxygenate Blends and Viscosity Models

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The pipeline transportation of bitumen is made difficult by excessive viscosities of the heavy oil. The current solution to this problem has been the addition of C_4+ paraffinic liquid hydrocarbons. There are however, a number of drawbacks to the use of this diluent. To overcome these drawbacks, the alternate use of MTBE (methyl-*tert*-butyl ether) and TAME (*tert*-amyl-methyl ether) gasoline additives as liquid solvent is investigated. With the potential for Alberta to become a substantial exporter of both bitumen and these ethers, the prospect of transporting two constituents simultaneously is promising. This can also be true for Iran in the future if export of bitumen and gasoline additive becomes a reality.

Two viscosity models were then derived and utilized to predict blend viscosities. The recommended model gave an accuracy of 2.1% average absolute deviation (AAD).

INTRODUCTION

Heavy oil and bitumen deposits represent a significant source of petroleum production. To fully utilize these resources, however, many difficulties not associated with the production of conventional crude oils must now be considered.

The most serious disadvantage in producing bitumen and heavy oil is the excessive viscosity of these fluids. As an example, Cold Lake bitumen has a viscosity of greater than 500,000 mPa.s (cP) at 4°C while the viscosity of a typical conventional oil may be 3–4 orders of magnitude lower [1]. To overcome this, the heavier oils are produced using a variety of enhanced oil recovery (EOR) techniques which use heat to reduce the viscosity [2]. Even once the bitumen has been removed from the reservoir, unique problems remain in the aspects of transportation and processing. To successfully transport the bitumen by pipeline, the viscosity must be substantially reduced. The current solution to this problem is the addition of liquid diluents to the heavy oil prior to transportation. The most common diluent used is C_4+, paraffinic liquid hydrocarbons obtained from natural gas processing. Although successful in reducing the viscosity of the bitumen to facilitate pipeline transportation, many drawbacks have been identified with the use of this solvent [3,4]. The drawbacks include: availability of the liquid hydrocarbon, insufficient buyers to purchase diluent upon completion of transportation and the possibility of producing asphaltene deposition. A superior liquid diluent would reduce the bitumen viscosity to the desired level without encountering asphaltene precipitation, while exhibiting a reasonable market value on its own.

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SELECTION OF OXYGENATING SOLVENTS

In a previous attempt to overcome these drawbacks, MTBE (methyl-*tert*-butyl ether) as an alternate to C_4+ hydrocarbon condensates was investigated [3]. The selection of MTBE was prompted by its increasing demand generated by its use as an octane enhancing/anti-knock blending agent for gasoline. The same selection criteria was used to identify TAME (*tert*-amyl-methyl ether) as a possible liquid diluent for the pipeline transportation of heavy oil and bitumen [5]. TAME is also used as additive in gasoline blending, although generally in smaller quantities. In both of the above investigations, Cold Lake bitumen was used as the heavy oil blended with the oxygenates [3,5]. This paper describes the results of the study on Athabasca bitumen as the heavy oil blended with the same oxygenates.

AREAS OF INVESTIGATION

The primary areas of interest to this study were the experimental determination of the effect of the oxygenates on the viscosity of the Athabasca bitumen, the case of separation of the two oxygenates from the blends and the possibility of asphaltene deposition.

The secondary objective of this study was to derive and correlate a reliable model for predicting the viscosity of the bitumen-diluent blends.

DESCRIPTION OF VISCOSITY MODEL

Due to the complex nature of bitumens, the majority of existing models used to predict the viscosity of bitumens and bitumen-diluent blends are empirical in nature. The primary model which is employed in this investigation utilizes a correlation of the component viscosities as a function of temperature and a mixing rule to determine the blend viscosities as a function of composition. For the purpose of viscosity modelling, the Athabasca bitumen-oxygenate blends were considered as pseudo-binary mixtures. A number of models were developed [6] and previously shown [3,4,6] to be accurate in the prediction of viscosities of hydrocarbon solvent-bitumen blends.

Correlation of Component Viscosities

The following is a modified form of the Walther [7] equation:

$$\log \log (\mu + 0.8) = b_1 + b_2 \log T, \qquad (1)$$

where μ = dynamic viscosity [mPa.s], T = temperature [K], b_1 and b_2 are characterization parameters unique to each component in the mixture. Equation 1 is used to correlate the temperature-viscosity data of the two oxygenates and the Athabasca bitumen.

A definite cross-correlation of the parameters b_1 and b_2 has been identified in the literature [8,9]. This cross-correlation can be represented by a linear relationship:

$$b_1 = \log \theta + (\log \Phi) b_2, \qquad (2)$$

where θ and Φ are generalized parameters used to represent a group of compounds. Inserting Equation 2 into Equation 1 yields the following correlation:

$$\log(\mu + 0.8) = \theta(\Phi T)^{b_1} \equiv \theta(\Phi T)^{b}. \qquad (3)$$

The values of θ and Φ have been regressed from a large set of experimental viscosity data and the generalized "best fit" values of the two constants were selected as $\Phi = 0.01$ and $\theta = 100$ [6]. The validity of Equations 1 and 3 are investigated against the experimental data determined in this study.

Calculation of Blend Viscosities

A wide variety of formulae used in liquid-mixture viscosity prediction exist. The simplest and most effective of these can be classified as additive equations. These equations are simply based on the weighted average of the component viscosities and thus, are very straight forward to use.

Other equations which are derived from the additive equations often attempt to account

for the interaction between the components in the mixture. To do this, a binary, or higher order, interaction term is employed. Also, this interaction term can be made a function of temperature or composition to better represent the experimental data. For the bitumen-diluent system being considered in this investigation, an equation of the following form is suggested [4,6]:

$$\log(\bar{\mu} + 0.8) = \sum_i \kappa_i \log(\mu_i + 0.8) + \sum_i \sum_j \kappa_i \kappa_j B_{ij}, \quad (4)$$

where $\bar{\mu}$ = predicted blend viscosity [mPa.s], κ_i = concentration term, B_{ij} = binary viscous interaction parameter (with $B_{ij} = B_{ji}$ and $i \neq j$). The binary interaction term requires a small set of experimental data to determine the best fit value or function.

The choice for the concentration term k_i in Equation 4 is the geometric mean of mass and mole fraction [5], calculated using: $\kappa_i = x_i(M_i/\overline{M})^{0.5}$, where x_i = mole fraction, M_i = molar mass and $\overline{M}$ = average molar mass. By combining the mixing rule given by Equation 4 with the concentration term described here and considering the system under investigation to be pseudo-binary, results in the following liquid-mixture viscosity equation:

$$\log(\bar{\mu} + 0.8) = x_S \left(\frac{M_S}{\overline{M}}\right)^{0.5} \log(\mu_S + 0.8) + x_B \left(\frac{M_B}{\overline{M}}\right)^{0.5} \log(\mu_B + 0.8) + 2x_S x_B \left(\frac{M_S M_B}{\overline{M^2}}\right)^{0.5} B_{SB}. \quad (5)$$

EXPERIMENTAL PROCEDURE

The experimental viscosity data was determined from a large set of liquid samples consisting of pure MTBE, TAME and Athabasca bitumen, along with binary blends of the oxygenates mixed with the bitumen in varying concentrations. To determine if the oxygenates appeared completely soluble in the Athabasca bitumen, the bitumen was blended with the MTBE in concentrations of 5% solvent up to 95% solvent (mass basis) and blended with the TAME in concentrations of 5% solvent up to 95% solvent (mass basis).

The viscosity of the bitumen-solvent blends was measured over the practical solvent concentration range which the bitumen would be diluted to for transport by pipeline. The two concentration ranges used were 20–35% MTBE (mass basis) and 15–35% TAME (mass basis). The viscosity data were then determined over a temperature range of 4–65°C.

Due to the fact that the viscosity of the pure oxygenates and undiluted bitumen may differ by roughly six orders of magnitude [4], two viscosity measuring procedures were required. The viscosity of the oxygenates was determined using a Cannon-Fenske routine viscometer (size 25: viscosity range of 0.4 to 2.0 cSt). To convert kinematic viscosity to dynamic viscosity, a Paar model DMA 48 electronic density meter was used. The viscosity measurments of the Athabasca bitumen and bitumen-solvent blends were performed using a Model RV8 viscometer [4,6] of Viscometers UK Ltd. (viscosity range of 10–10^6 mPa.s).

The molar mass of the Athabasca bitumen sample is required for conversion between mass and mole basis, both of which are utilized in the viscosity models. To determine the molar mass of the bitumen, a Corona Wescan Molar Mass Apparatus (Model 232A) using the procedure of vapor pressure osmometry is employed [4].

To determine the ease of separation of the oxygenates from the solvent-bitumen blends, a simple distillation apparatus (ASTM D 267) [10] was assembled. The experimental results were used to construct a distillation curve of temperature versus mass distilled of solvent-bitumen blends at atmospheric pressure. Two mixtures consisting of 30% (mass basis) MTBE-Athabasca bitumen and 30% (mass basis) TAME-Athabasca bitumen were distilled using the described apparatus. The amount of distillate removed was continuously monitored by a sensitive balance.

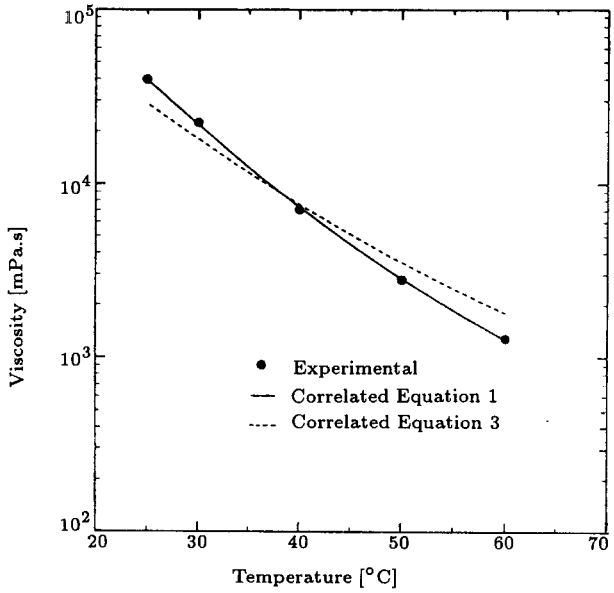

Figure 1. Viscosity results for Athabasca bitumen.

RESULTS AND DISCUSSION

Correlation of Component Viscosities

The experimental viscosity results are presented along with the results of correlation for the unblended Athabasca bitumen, MTBE and TAME. The temperature-viscosity data obtained experimentally for the two pure oxygenates are displayed in Figure 1 and the data obtained for the bitumen are displayed in Figure 2. The characterization parameters of Equations 1 and 3 are used to correlate the experimental data and these values are presented in Table 1. The characterization parameter b in Equation 3 is regressed using the experimental data and generalized constants ($\theta = 100$ and $\Phi = 0.01$).

It can be seen from Table 1 that the absolute average deviation (AAD) for both models remains relatively low, which indicates that they accurately represent the experimental data. The only exception is the high AAD for Equation 3 correlating the viscosity of the Athabasca bitumen. This average error of greater than 20% indicates that the generalized one-parameter Equation 3 is not sufficiently accurate to model the unblended bitumen. The results in Table 1, however, indicate that Equation 1 is satisfactory to model the effect of temperature on viscosity for both the pure oxygenates and bitumen.

Calculation of Blend Viscosities

With the temperature-viscosity data of both components in the mixture accurately correlated using Equation 1, it is now possible to utilize Equation 5 to predict the viscosity of the bitumen-diluent blends. In order to do this, the interaction parameter in Equation 5 must first be calculated. The experimental viscosity data were used to back calculate an interaction parameter for each blend composition at every temperature investigated. This set of calculated interaction parameters were then regressed using two different correlative methods: Model 1 correlates B_{SB} as a function of temperature, and Model 2 as a function of temperature and composition.

The following relationships demonstrate the correlations of the binary interaction parameters of Models 1 and 2 [4]:

$$Model\,1 : B_{SB} = a_1 + a_2(T - 273.15)$$
$$Model\,2 : B_{SB} = c_1 + c_2(T - 273.15) + c_3 S, \quad (6)$$

where B_{SB} = binary interaction between sol-

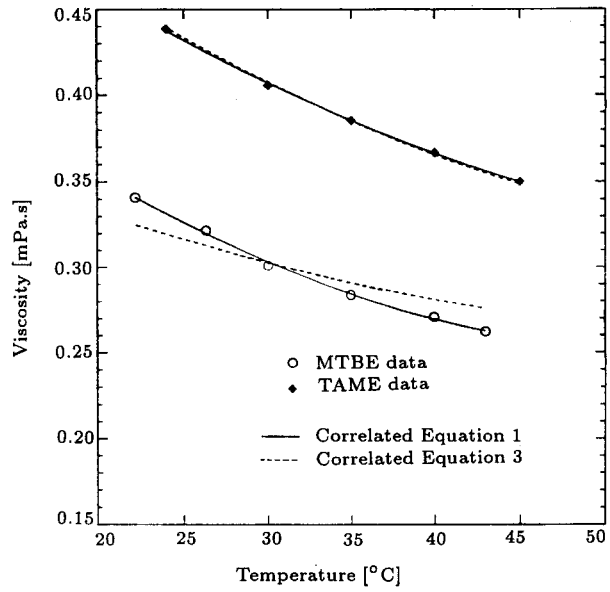

Figure 2. Viscosity results for MTBE and TAME.

vent and bitumen, T = temperature [K], S = solvent concentration [mass %], a_1, a_2 = empirical parameters, c_1, c_2, c_3 = empirical parameters.

The calculated interaction parameters of Equation 5 along with the linear correlation of the data using Models 1 and 2 can be seen in Figure 3. Figure 3 demonstrates that the additional parameter utilized in Model 2 enhances the accuracy of the correlation.

Liquid-Mixture Viscosity Predictions

Figure 4 displays the results of Equation 5 using the two interaction parameter modelling approaches versus the MTBE-Athabasca bitumen blend viscosities determined experimentally. It can be seen that Model 2 is much more accurate in predicting blend viscosities than Model 1.

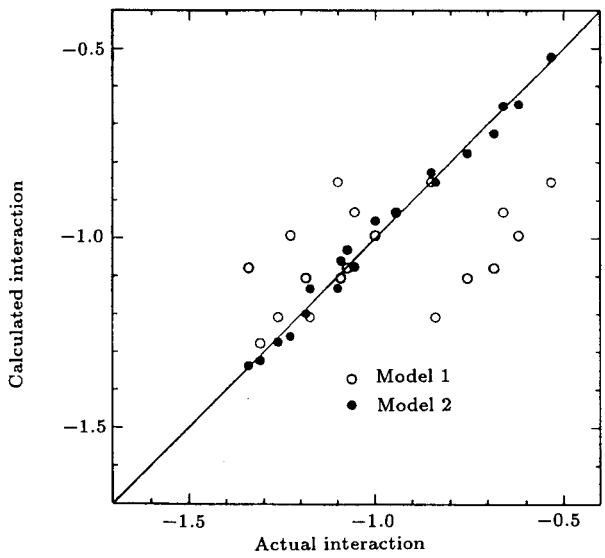

Figure 3. Correlation results for Models 1 and 2.

Figure 5 displays the results of Equation 5 using the two interaction parameter modelling approaches versus the TAME-Athabasca bitumen blend viscosities determined experimentally. It is again displayed that Model 2 is considerably more accurate. The quality of these numerical agreements is presented in Table 2. These results compare favorably to calculations without consideration of an interaction parameter, where errors up to 100% AAD have been encountered [3,4]. These calculations are based on the molar mass of the Athabasca bitumen sample being experimentally determined as 602 g/mol ± 10%.

By applying the verified viscosity model, Equation 5, with the interaction term calculated using Model 2, it is determined that a 25.9% (mass solvent) MTBE-Athabasca bitumen blend, and 27.5% (mass solvent) TAME-Athabasca bitumen will meet the required pipeline specifications; the specifications call for the blend to have a viscosity lower than 250 cSt at 4°C with an API gravity of 21° (approximately 269 mPa.s).

Extended Areas of Interest

Two simple distillations of Athabasca bitumen-diluent mixtures (30% mass MTBE and 30% mass TAME) were performed, with the results presented as a distillation curve of temperature versus mass of distillate, shown in Figures 6 and 7. Figure 6 shows that nearly all of the MTBE was separated from the blend at a vapor temperature of just over 50°C. Figure 7 shows that separation of TAME from the blend caused a gradual climb in the vapor

Table 1. Correlation results (Equations 1 and 3) of viscosity data of pure components.

	Equation 1			Equation 3	
	b_1	b_2	%ADD*	b	%AAD
MTBE	27.1854	−11.5068	0.4	−6.9989	3.3
TAME	14.2598	−6.1843	0.1	−6.4082	0.3
Athabasca Bitumen	9.4567	−3.5538	2.2	−2.8460	24.0

*$\%AAD = \frac{1}{N}\sum\left|\frac{\mu_{cal}-\mu_{exp}}{\mu_{exp}}\right| \times 100$

Table 2. Correlation results and viscosity predictions of Models 1 and 2.

	Model 1			Model 2			
	a_1	a_2	%ADD	c_1	c_2	c_3	%AAD
MTBE - Athabasca	−1.277	1.73×10^{-2}	11.4	−0.339	1.24×10^{-2}	-2.81×10^{-2}	1.7
TAME - Athabasca	−1.134	1.41×10^{-2}	17.7	−0.318	1.27×10^{-2}	-3.05×10^{-2}	2.4

temperature from 80–85°C. The small climb in boiling point plateaus observed for the TAME blend could be merely caused by the increased impurities in the TAME samples as compared to the MTBE samples (compare purities of 99.5% MTBE to 94% TAME). The ultimate recovery of oxygenates in both cases is nearly 90%. This is satisfactory considering the single-stage distillation was an open system with the potential for a loss of distillate.

Also of interest to this study was the possibility of encountering asphaltene deposition due to the addition of the liquid diluent. It can be stated that no such separation of a solid phase was observed, either as a precipitate or in suspension, in concentrations up to 95% (mass) MTBE-Athabasca bitumen and 95% (mass) TAME-Athabasca bitumen.

CONCLUSIONS

To overcome some of the difficulties associated with using a conventional liquid diluent in the transportation of heavy oil, a study into the alternate use of MTBE and TAME was conducted.

Two correlations were evaluated using the experimental temperature-viscosity data of this experiment: Equation 1 demonstrated an accuracy of 0.9% AAD versus the accuracy of Equation 3 at 9.2% AAD. Two models were then utilized to predict blend viscosity, with

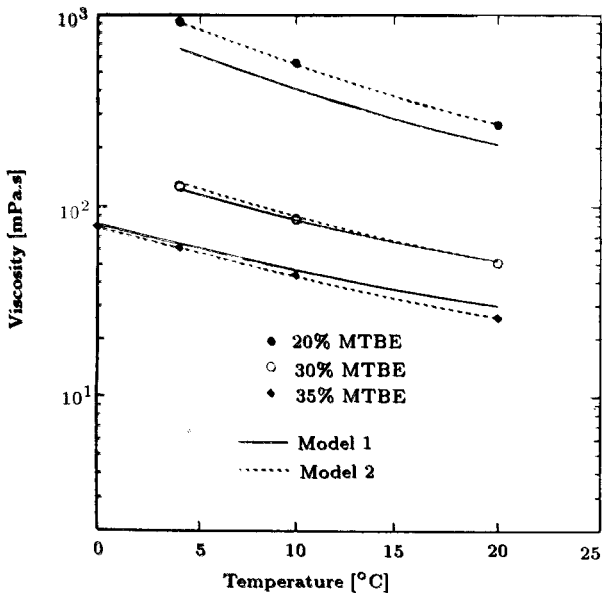

Figure 4. Viscosity results for Athabasca bitumen-MTBE blends.

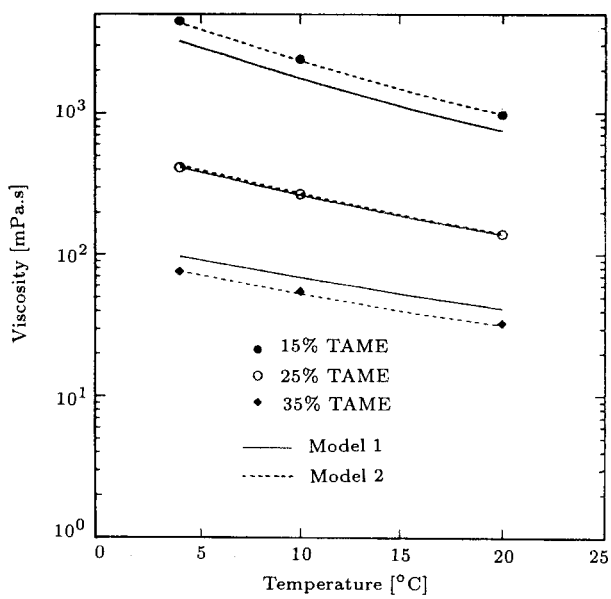

Figure 5. Viscosity results for Athabasca bitumen-TAME blends.

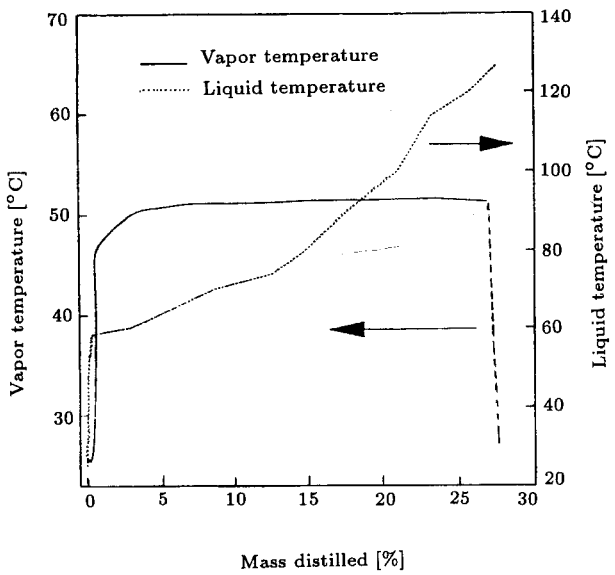

Figure 6. Distillation curve of 30% (mass) Athabasca bitumen-MTBE blend.

the accuracy of Model 2 (2.1% AAD), being superior to Model 1 (14.6% AAD).

The test of ease of separation of the oxygenating solvents from the bitumen, using a simple distillation apparatus, reveals that the bulk of the diluent can be removed without difficulty. Furthermore, by visual observation it was noted that no asphaltene precipitates were formed in all the mixtures which were studied in this research project. It would appear that the addition of the oxygenates to the Athabasca bitumen eliminates, or delays, the onset of asphaltene deposition.

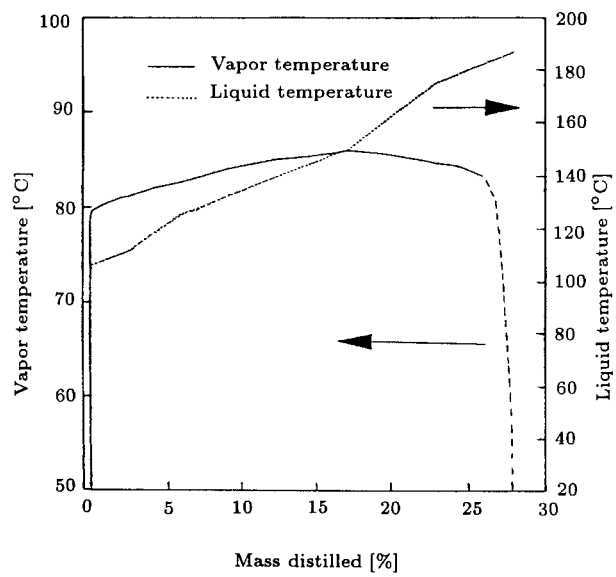

Figure 7. Distillation curve of 30% (mass) Athabasca bitumen-TAME blend.

FUTURE WORK

Further investigation into this topic will include extension into various different bitumen-diluent systems. These mixtures will consist of Cold Lake and Athabasca bitumens blended with several additional solvents. An investigation into alternate modelling approaches will also be detailed. Also, a more accurate detection of asphaltene precipitates could establish more significant phase separation results.

ACKNOWLEDGMENTS

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NOMENCLATURE

AAD	average absolute deviation
a_1, a_2	regression constants
b	viscosity correlation parameter
b_1, b_2	viscosity correlation parameters
B	binary viscous interaction term
c_1, c_2, c_3	regression constants
M	molar mass [g/mol]
$\overline{M}$	average molar mass [g/mol]
N	number of experimental points
n	number of components in mixture
S	solvent concentration [% mass]
T	absolute temperature [K]
x	mole fraction

Greek Symbols

θ	generalized viscosity constant
κ	concentration term

μ	dynamic viscosity (mPa.s or cP)
$\bar{\mu}$	predicted blend viscosity (mPa.s)
Φ	generalized viscosity constant

Subscripts

B	bitumen
cal	calculated
exp	experimental
i	component i
j	component j
S	solvent

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