



## Correlation for viscosities of pure liquids at high pressures



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### ABSTRACT

An accurate model for the viscosities of nonpolar and polar liquids at high pressure based on the Eyring's absolute rate theory and the equation of state has been proposed by Martins et al. in 2003. One characteristic of this model is requiring two adjustable parameters at each temperature, which limits its application. In this work, we modified their model by establishing correlations between the adjustable parameters and temperature to improve its predictive potential. The present model coupled with Soave-Redlich-Kwong equation of state was applied to correlate the viscosities of 30 compounds including alkanes, alkenes, aromatics, alcohols, oxygen, argon and nitrogen at temperatures from 65 K to 460 K and pressures from 0.1 MPa to 253.1 MPa. The calculated values from the present model agree well with the experimental data in all cases, with the average absolute relative deviations lower than 3.7%.

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### 1. Introduction

Organic solvents including alkanes, alkenes, aromatics and alcohols play an important role in the industrial processes such as chemical reaction, gas absorption, extraction and so on. Viscosity is one of the most important thermophysical properties of these substances, which is required for designing the industrial processes that involve fluid movement or dissolution of other components in them. Compared with the scattered experimental data, accurate viscosity models are more useful in application. Although many viscosity models for liquids have been proposed, but most of them just applicable to low pressure as reviewed in literature [1], such as the corresponding states theory [2,3], the Vogel-Fulchner-Tammann equation [4]. In the last decades, several models have been developed to describe the viscosities of liquids at high pressure. Quinones-Cisneros et al. [5] proposed a friction-theory viscosity model based on the classical mechanics and the Van der Waals theory of fluids, which is applicable to gas and liquid. In their model, the van der Waals repulsive pressure term and attractive pressure term were obtained from equation of state. The friction-theory viscosity model has been applied to alkanes and alcohols et al. [5–7] coupled with the cubic equation of state or the statistical associating fluid theory equations of state (SAFT). Allal et al. [8] proposed a free-volume viscosity model by establishing a connection between the molecular free volume and viscosity, which also is applicable to

different fluids in the gas and liquid phase [8–13]. Ciotta et al. [14] proposed an extend hard-sphere model for dense fluids based on the model of Assael et al. [15], and applied it to n-alkanes. However, these semi-empirical models always involve complex calculations for the determination of their adjustable parameters or limited application range as stated in literatures [16–18]. Two empirical viscosity models with the advantages of simplicity and good predictive capability were proposed in recent years. One is proposed by Yarranton and Satyro [18–20] based on correlating viscosity to density and using Peng–Robinson equation to calculate the density. Their model was modified and coupled with SAFT + cubic equation of state by Polishuk in order to improve the predictive capability [16, 17,21]. Another one is proposed by Martins et al. [22] based on the Eyring's absolute rate theory. In this model, the difference of the molar activation energy for flow at given condition and in the reference state was considered to be equal to the difference of the molar Helmholtz free energy which was obtained using cubic equation of state, such as Peng–Robinson (PR) equation, Soave–Redlich–Kwong (SRK) equation, and Peng–Robinson–Stryjek–Vera (PRSV) equation. This model gave very good agreement with the experimental viscosity data for 49 different compounds in liquid phase at pressures up to 250 MPa. The overall average relative deviation from experimental data was 1.2%. However, Martins et al.'s model has a disadvantage that it requires two adjustable parameters for each temperature.

In this work, we present a modification of Martins et al.'s model by establishing a connection between its adjustable parameters and temperature in order to improve its predictive potential and make it more easily implemented. The new model coupled with SRK equation was

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tested by experimental viscosity data of 30 liquids at temperatures from 65 K to 460 K and pressures from 0.1 MPa to 253.1 MPa.

## 2. Viscosity model

As described in the Eyring's absolute rate theory [23], the dynamic viscosity of liquid  $\eta$  can be calculated by

$$\eta = \frac{hN}{V} \exp\left(\frac{\Delta F^*}{RT}\right) \quad (1)$$

where  $h$  is Planck's constant,  $\Delta F^*$  is the molar energy of activation for flow,  $N$  is Avogadro's number,  $V$  is molar volume,  $R$  is the gas constant,  $T$  is temperature. The viscosity of fluid in the reference state  $\eta_0$  can be written as

$$\eta_0 = \frac{hN}{V_0} \exp\left(\frac{\Delta F_0^*}{RT}\right) \quad (2)$$

where  $V_0$  is molar volume of liquid in the reference state. Combining Eqs. (1) and (2), we can obtain the following formula

$$\eta = \eta_0 \frac{V_0}{V} \exp\left(\frac{\Delta F^* - \Delta F_0^*}{RT}\right) \quad (3)$$

The difference of the molar activation energies  $\Delta F^* - \Delta F_0^*$  is considered to be equal to the difference of the molar Helmholtz free energy  $\Delta A$ . Therefore, Eq. (3) can be rewritten as

$$\eta = \eta_0 \frac{V_0}{V} \exp\left(\frac{\Delta A}{RT}\right) \quad (4)$$

where  $\Delta A$  is the deviation of the molar Helmholtz free energy of the fluid at given condition from that in the reference state. The ratio of molar volume is calculated by

$$V_0/V = 1 + B_1(T)p + B_2(T)p^2 \quad (5)$$

where  $B_1(T)$  and  $B_2(T)$  are adjustable parameters related to temperature. In Martins et al.'s model, at each temperature, the values of  $B_1$  and  $B_2$  should be obtained by fitting to the experimental data. In order to improve its predictive capacity, we used two functions of reduced temperature to calculate  $B_1$  and  $B_2$ :

$$B_i = \exp[a_i + b_i T_r^{c_i}] \quad (i = 1, 2) \quad (6)$$

where

$$T_r = \frac{T}{T_c} \quad (7)$$

where  $a_i$ ,  $b_i$  and  $c_i$  are adjustable parameters, which can be obtained by fitting Eq. (6) to the  $B_i$  at different temperatures;  $T_c$  is critical temperature. When chose the viscosity of dilute gas as the reference state viscosity and combine Eqs. (4)–(7), we can get

$$\eta = \eta_0 [1 + \exp(a_1 + b_1 T_r^{c_1})p + \exp(a_2 + b_2 T_r^{c_2})p^2] \exp\left(\frac{A^R}{RT}\right) \quad (8)$$

where  $A^R$  is the residual molar Helmholtz free energy, which is obtained by equation of state. In this work, the modified Chapman-Enskog theory proposed by Chung et al. [24] was used to calculate the viscosity of dilute gas  $\eta_0$  (Pa · s), which is given by

$$\eta_0 = 0.40785 \times 10^{-5} \times \frac{\sqrt{M_w T}}{V_c^{2/3} \Omega^*(T^*)} F_c \quad (9)$$

where  $M_w$  ( $\text{g} \cdot \text{mol}^{-1}$ ) is the molecular weight,  $V_c$  ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ) is the critical volume,  $F_c$  is the correction factor,  $\Omega^*$  is the reduced collision integral.  $F_c$  can be calculated by

$$F_c = 1 - 0.2756\omega + 0.059035\mu_r^4 + \kappa \quad (10)$$

where  $\omega$  is the acentric factor,  $\mu_r$  is the dimensionless dipole moment,  $\kappa$  is the parameter account for hydrogen bonding formation. These parameters can be obtained from literature [25–27].  $\Omega^*$  can be obtained using the empirical correlation [28]:

$$\Omega^* = \frac{1.16145}{T^{*0.14874}} + \frac{0.52487}{\exp(0.77320T^*)} + \frac{2.16178}{\exp(2.43787T^*)} - 6.435 \times 10^{-4} \times T^{*0.14874} \sin(18.0323T^{*-0.7683} - 7.27371) \quad (11)$$

where  $T^* = 1.2593T_r$ .

Compared with other complex equations like the SAFT equations, the cubic equation of states are easier to implement although the

**Table 1**

Summary of selected literature data for the viscosity of liquids.

Liquid	T/K	p/MPa	Number of data	Reference
Methane	100–140	0.1–50	43	[30]
Ethane	100–210	0.1–60	126	[31]
Propane	90–240	0.1–100	281	[32]
n-Butane	323–348	13.3–69.2	33	[33]
	280–340	2–70	72	[34]
n-Pentane	318–323	7.5–69.8	26	[33]
	320–380	2–50	68	[34]
	313–328	5–24.6	10	[35]
	303	5.6–251.3	14	[36]
n-Hexane	313–373	0.2–65.9	46	[33]
	380–420	2–40	42	[34]
	303–348	0.1–250	37	[36]
n-Heptane	300–360	0.1–50	66	[34]
	303–343	0.1–100	18	[37]
	303–348	0.1–248.9	46	[38]
n-Octane	323–448	8–66.5	47	[33]
	320–360	0.1–50	40	[34]
	303–348	0.1–253.1	48	[36]
n-Nonane	300–420	0.1–50	221	[34]
n-Decane	280–440	0.1–35	210	[34]
	303–323	0.1–238.8	30	[36]
	310.9	1.4–55.2	20	[39]
	297–373	0.1–24.6	36	[40]
n-Undecane	300–460	0.1–50	182	[34]
n-Dodecane	300–460	0.1–50	182	[34]
	293–373	0.1–100	30	[41]
Benzene	290–350	0.1–40	98	[34]
	298–348	0.1–177.6	30	[42]
Toluene	295–380	0.1–40	140	[34]
	303–348	0.1–252	46	[36]
	298–363	0.1–100	30	[43]
Ethylbenzene	300–400	0.1–40	85	[34]
Cyclohexane	290–350	0.1–50	119	[34]
Methylcyclohexane	290–400	1–50	140	[34]
	298–363	0.1–100	30	[43]
Methanol	290–330	0.1–80	70	[34]
	298.15	0.1–71.8	11	[44]
Ethanol	270–350	0.1–100	98	[34]
	298.15	0.1–71.8	11	[44]
1-Propanol	320–420	0.1–50	55	[34]
	298.15	0.1–71.8	11	[44]
2-Propanol	430–440	5–80	22	[34]
	303–343	0.1–100	18	[45]
Isobutane	310–380	2–50	85	[34]
Isopentane	280–380	0.1–60	113	[34]
Isooctane	290–400	0.1–50	137	[34]
n-Hexene	280–370	0.1–45	135	[34]
n-Heptene	300–380	0.1–50	126	[34]
n-Octene	300–380	0.1–50	127	[34]
Nitrogen	65–100	0.1–50	139	[34]
Argon	90–120	0.5–50	110	[46]
Oxygen	75–115	0.1–50	177	[34]

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