

# Gibbs Energy Additivity Approaches in Estimation of Dynamic Viscosities of n-Alkane-1-ol

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**Abstract.** Alcohols are solvents for organic and inorganic substances. Dynamic viscosity of liquid is important transport properties. In this study models for estimating n-alkan-1-ol dynamic viscosities are correlated to the Martin's rule of free energy additivity. Data available in literatures are used to validate and support the proposed equations. The dynamic viscosities of n-alkan-1-ol can be easily estimated from its carbon numbers ( $n_c$ ) and temperatures ( $T$ ). The bias, average absolute deviation and coefficient of determination ( $R^2$ ) in estimating of n-alkan-1-ol are -0.17%, 1.73% and 0.999, respectively. The dynamic viscosities outside temperature between 288.15 and 363.15 K may be possibly estimated by this model but accuracy may be lower.

## 1. Introduction

Alcohols are solvents for organic and inorganic substances. Recently, alcohols have been proposed as an alternatives as oxygenated fuel. Oxygenated fuel is used to help fuel burn more efficiently and cut down on some types of atmospheric pollution.[1] Viscosity of liquid is important for equipment design, heat and mass transfer. There were many published mathematical models for prediction of viscosity of the liquids, including vegetable oils. The Andrade equation (Eq.1) was a good equation that correlates dynamic viscosity ( $\eta$ ) to the free energy of viscous flow ( $\Delta G$ ) and absolute temperature ( $T$ ).[2, 3]

$$\eta = A_0 e^{-\Delta G/RT} \quad (1)$$

Or

$$\ln \eta = A + \frac{B}{T} \quad (2)$$

where  $A_0$  and  $A$  are constant and  $\ln A_0$ , respectively.

$B$  is  $\Delta G/RT$

$R$  is universal gas constant.

However, Eq.1 just correlated the dynamic viscosity to temperature without structural information. In this study, attention was paid on the Martin's rule of free energy additivity. The free energy of viscous flow for n-Alkane-1-ol in Eq.1 was expanded to the enthalpy and entropy forms.

## 2. Theory

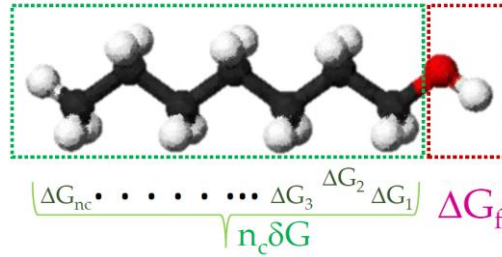


Figure 1 correlation of free energy additivity and n-alkan-1-ol molecular structure.

From figure 1 show a compound having the molecular structure of  $\text{CH}_3(-\text{CH}_2)_{n_c}-1-f$ . Martin [4] divided the molecule into different groups:  $f$ ,  $\text{CH}_2$ ,  $\text{CH}_3$ . The free energy of transfer from solution to gas ( $\Delta G$ , in gas chromatography) of the molecule was derived from the sum of the free energies of all contributed groups; ie, the free energy contribution from the structural groups are additive.

$$\Delta G = \Delta G_f + \Delta G_1 + \Delta G_2 + \dots + \Delta G_{n_c} \quad (3)$$

$\Delta G_1, \dots, \Delta G_{n_c}$  are the free energies of the methylene and methyl groups, which are not very different. Thus, they are average to  $\Delta G$  and Eq.3 is shortening to Eq.4.

$$\Delta G = \Delta G_f + n_c \delta G \quad (4)$$

where  $\Delta G_f$  is the free energy of the functional group,  $f$ ;  $\Delta G$  is the change in free energy/carbon atom;  $n_c$  is the number of carbon atoms.

Substitution Eq.4 into Eq.1 and expansion the free energy to enthalpy and entropy forms ( $G=H-TS$ ),

$$\ln \eta = \ln A - \frac{\Delta H_f}{RT} + \frac{\Delta S_f}{R} - \frac{n_c \delta H}{RT} + \frac{n_c \delta S}{R} \quad (5)$$

or

$$\ln \eta = a + b n_c + (c + d n_c) \frac{1}{T} \quad (6)$$

where  $a = \ln A + \frac{\Delta S_f}{R}$ ,  $b = \frac{\delta S}{R}$ ,  $c = -\frac{\Delta H_f}{R}$  and  $d = -\frac{\delta H}{R}$

Eq.6 is used for estimation of dynamic viscosity of n-alkan-1-ol at several temperatures.

## 3. Materials and Methods

### 3.1 Dynamic viscosity data

The dynamic viscosities values of n-alkan-1-ol were obtained from the report of Mokhtaram et al.[5] (propanol and butanol) and Baltazer et al.[6]. (pentanol, hexanol and heptanol). The dynamic viscosities were measured by using Anton Paar Automated Micro Viscometer (AMVn).

### 3.2 Numeric constants of Eq.6

All the four numeric constants of Eq.5 were solved by multiple linear regression according to Phankosol et al. [3, 7, 8] as shown in Eq.7.

$$\ln \eta = -5.008 + 1481.8n_c - (0.3925 + 194.07n_c) \frac{1}{T} \quad (7)$$

### 3.4 Statistical analysis

The percent average absolute deviations (AAD (%)) were calculated from Eq.8.

$$AAD(\%) = \sum_{i=1}^N \left| \frac{\eta_{exp} - \eta_{cal}}{\eta_{exp}} \times 100 \right| / N \quad (8)$$

where *exp* stands for experimental value reported elsewhere, *cal* is the calculated value and *N* is the number of data points.

## 4. Results and Discussion

Percent differences between the calculated by Eq.7 and literature dynamic viscosities values are listed in the parentheses, at 288.15-363.15 K are summarized in Table 1. The estimated dynamic viscosities values for n-propanol, n-butanol, n-pentanol, n-hexanol and n-heptanol agrees well with the literature values. The highest absolute difference is 6.65% (Propanol at 333.15 K). The Bias and AAD (%) were -0.17% and 1.73%, respectively.

Table 1 Estimated dynamic viscosities (mPa.s) of n-alkan-1-ol at 288.15–363.15 K

T (K)	Propanol[5] ( <i>n<sub>c</sub></i> =3)		1-Butanol[5] ( <i>n<sub>c</sub></i> =4)		1-Pentanol[6] ( <i>n<sub>c</sub></i> =5)		1-Hexanol[6] ( <i>n<sub>c</sub></i> =6)		1-Heptanol[6] ( <i>n<sub>c</sub></i> =7)	
	$\eta_{cal}$ (mPa.s)	D (%)	$\eta_{cal}$ (mPa.s)	D (%)	$\eta_{cal}$ (mPa.s)	D (%)	$\eta_{cal}$ (mPa.s)	D (%)	$\eta_{cal}$ (mPa.s)	D (%)
288.15	3.52	3.97	3.52	-3.80	4.66	-	6.17	-	8.18	-
293.15	2.35	2.42	3.08	-2.31	4.03	-0.01	5.28	1.54	6.91	2.91
298.15	2.09	1.31	2.71	-3.85	3.50	-0.59	4.54	0.85	5.88	2.02
303.15	1.86	0.51	2.39	-3.19	3.06	-1.12	3.92	0.31	5.02	1.34
308.15	1.67	0.08	2.12	-2.48	2.68	-1.65	3.40	-0.15	4.31	0.82
313.15	1.50	1.54	1.88	-1.92	2.36	-2.13	2.97	-0.55	3.72	0.45
318.15	1.35	2.22	1.68	-1.30	2.09	-2.59	2.60	-0.87	3.23	0.23
323.15	1.22	2.59	1.51	-0.75	1.85	-2.99	2.28	-1.10	2.81	0.11
328.15	1.11	3.67	1.35	0.18	1.65	-3.40	2.02	-1.25	2.46	0.14
333.15	1.01	6.65	1.22	1.78	1.48	-3.79	1.79	-1.31	2.16	0.24
338.15	0.92	-	1.10	-	1.32	-4.14	1.59	-1.35	1.90	0.47
343.15	0.84	-	1.00	-	1.19	-4.46	1.42	-1.29	1.68	0.84
348.15	0.77	-	0.91	-	1.08	-	1.27	-1.15	1.50	1.26
353.15	0.71	-	0.83	-	0.97	-	1.14	-0.98	1.33	1.79
358.15	0.66	-	0.76	-	0.88	-	1.03	-0.78	1.19	2.36
363.15	0.61	-	0.70	-	0.80	-	0.93	-0.51	1.07	3.00
Overall	Bias	<b>2.50</b>		<b>-1.76</b>		<b>-2.44</b>		<b>-0.57</b>		<b>1.20</b>
	AD (%)	<b>2.50</b>		<b>2.16</b>		<b>2.44</b>		<b>0.93</b>		<b>1.20</b>

The correlation between the reported experimental dynamic viscosities of Mokhtaram et al.[5] and Baltazer et al.[6] and estimated values using Eq.7 (61 data points) show in figure 2 was linear with the slope of 0.982 and intercept at 0.0427. The  $R^2$  and standard error are 0.999 and 0.022, respectively.

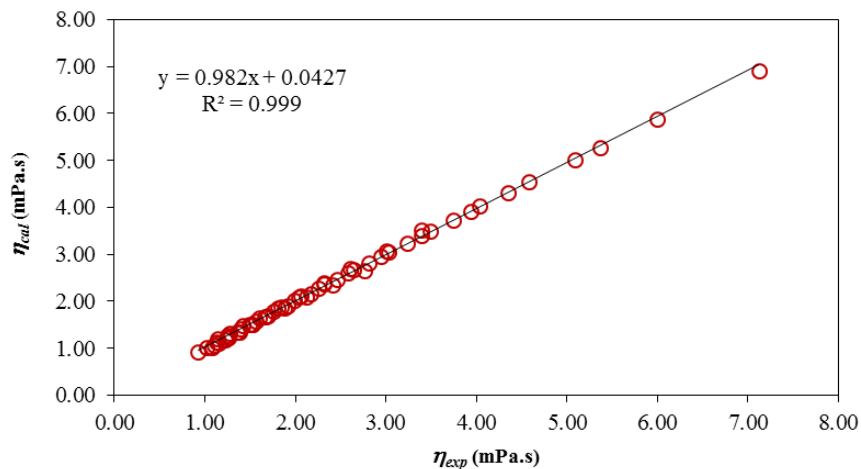


Figure 2 Correlation of the estimated dynamic viscosities ( $\eta_{cal}$ ) to the experiment values ( $\eta_{exp}$ ) [3,10] of n-alkan-1-ol at 288.15-363.15 K.

## 5. Conclusions

This work, the total free energy is then related to physical property of the n-alkan-1-ol via an existing equation. Thus, the derive equation can then be used to estimate dynamic viscosities of the n-alkan-1-ol at different temperatures with good accuracy. The dynamics viscosities values outside of this temperature range may be possibly predicted by the correlation but the accuracy may be lower.

## Acknowledgements

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