



Sensitivity of Viscosity Arrhenius-Type Equation to Density of Liquids

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Numerous empirical or semi-empirical equations are proposed in the literature to describe the temperature dependence of fluids viscosity. This paper aims to contribute to this research axis by investigating the effect of density of liquids on the modeling of liquid viscosity upon temperature. We focused for that on the Arrhenius-type equation. Using experimental data set of pure solvents from the literature, this study is based on the classification of heavy liquid *versus* light liquid. Thus, statistical tests and econometric estimations showed that there is strong evidence that this classification affect significantly the distribution of the Arrhenius-type equation parameters and the modeling of the viscosity-temperature dependence. It is suggested that new specific coefficient values of the simplified Arrhenius-type equation taking into consideration the said effect and allowing better estimation accuracy. This result is important for the accuracy in the estimation of the models' parameters for chemical and industrial processes and designs. It could also pave the way to investigate more accurate values of the equation's parameters when the natures of fluids are classified differently.

Keywords: Viscosity, Pure liquid, Arrhenius behaviour, Correlation, Statistics.

INTRODUCTION

Viscosity is one of the most considered transport properties for the design and the optimization of several industrial processes such as food production, chemical industry, cosmetics and pharmaceuticals, *etc.* Viscosity is essential property for hydraulic calculations of fluid transport and for energy transference computation [1-6].

Theoretical description of viscosity is quite complex. For that, numerous methods have been proposed in the literature, focused particularly on modeling the variation of viscosity with temperature. These methods are essentially based on the Eyring theory [1,2,7-9].

In this context and knowing the importance of the accuracy in the estimation of the viscosity-temperature dependence, which may affect considerably the design and the optimization of several industrial processes, the aim of this paper is to give additional estimation accuracy by analyzing the effect of density of liquids on modeling the viscosity-temperature dependence. Our analysis will be based essentially on the Arrhenius type equation and the simplified Hajkacem-Ouerfelli equations [10,11].

Due to the complex nature of fluid, there is no comprehensive theory of viscosity. Indeed, several methods have been proposed in the literature such as the distribution function theory of Kirkwood *et al.* [12], the molecular dynamic

approach of Cumming and Evans [13] and the reaction rate theory of Eyring [14-16].

Particular attention has been paid to the analysis of the viscosity-temperature dependence. Thus, given that temperature dependence of the internal frictional coefficient of fluids is determined both by the thermal changes of the free volume and by thermodynamics of intermolecular interactions, the modeling of the viscosity-temperature dependence is generally expressed based on at least two-parameters.

The most important expressions proposed in the literature for modeling the liquid dynamic viscosity (η) upon temperature (T) can be summarized as following [10]:

$$\ln \eta = A + \frac{B}{T+C} + a \cdot \log T + b \cdot T + c \cdot T^2 + \frac{D}{T^2} + \frac{E}{T^3} + \frac{F}{T^n} \quad (1)$$

Following this representation, the viscosity-temperature dependence can be classified according to two main families for liquid systems, based on their linear or non-linear behaviour of the logarithm of shear viscosity ($\ln \eta$) *versus* the reciprocal of absolute temperature ($1/T$).

The first family suggests a linear behaviour of the temperature-viscosity dependence which is generally fitted with the Arrhenius-type equation in the logarithmic. Thus, the relationship between the logarithm of shear viscosity ($\ln \eta$) and the reciprocal of absolute temperature ($1/T$) is assumed to be as following:

$$\ln \eta = \ln A_s + \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (2)$$

where R is the gas constant, E_a is the activation energy and $\ln A_s$ is the pre-exponential factor. E_a and $\ln A_s$ are the Arrhenius equation parameters assumed to be independent of temperature.

The second family considers non-linear behaviour of the temperature dependence of dynamic viscosity which leads to consider the Vogel-Fulcher-Tammann-type equation as following [10,17-19]:

$$\ln \eta = \ln A_0 + \frac{E_0}{R} \left(\frac{1}{T - T_0} \right) \quad (3)$$

where A_0 , E_0 and T_0 are constants.

Recently, based on graphical illustration of the Arrhenius-type equation, Haj-Kacem *et al.* [10] defined the Arrhenius temperature parameter (T_A) deduced from the intercept with the abscissa axis related to the reciprocal absolute temperature to the following form.

$$T_A = \frac{-E_a}{R \ln(A_s)} \quad (4)$$

Using experimental data on viscosity for some pure liquids and binary liquid mixtures over different temperature ranges at atmospheric pressure and based on the econometric estimation of the eqn. 5, Haj-Kacem *et al.* [10,11] have found significant statistical correlation between the two parameters (E_a) and ($\ln A_s$) following eqn. 6 and 7:

$$\ln T^* = \alpha_1 + \alpha_2 \ln T_A \quad (5)$$

$$E_a = \lambda \cdot R \times (-\ln A_s)^{\alpha_0} \quad (6)$$

$$\ln A_s = - \left(\frac{E_a}{\lambda R} \right)^{\frac{1}{\alpha_0}} \quad (7)$$

where $\lambda = e^{\frac{\alpha_1}{1-\alpha_2}}$ indicates the dimension's equation, α_1 and α_2

are the models' parameters of the regression of $\ln \left(\frac{E_a}{R} \right)$ on

$\ln T_A$ and $\alpha_0 = \frac{-\alpha_2}{1-\alpha_2}$.

Thus, the Hajkacem-Ouerfelli [10] expressions allow the simplification of the Arrhenius-type equation by using a single parameter (eqn. 8 or 9) instead of two ones (eqn. 3).

$$\ln \eta = \ln A_s + \lambda (-\ln A_s)^{\alpha_0 \left(\frac{1}{T} \right)} \quad (8)$$

$$\ln \eta = - \left(\frac{E_a}{\lambda R} \right)^{\frac{1}{\alpha_0}} + \frac{E_a}{\lambda R} \left(\frac{1}{T} \right) \quad (9)$$

For practical use and based on econometric estimations, Haj-Kacem *et al.* [10] suggested the following simplified equations with good approximation for numerous classical solvents obeying to the viscosity Arrhenius-type equation ($6 < E_a < 30$) and ($-17 < \ln(A_s) < -10$):

$$\ln \eta = \ln A_s + (-\ln A_s)^{2.933} \left(\frac{1}{T} \right) \quad (10)$$

$$\ln \eta = - \ln \left(\frac{E_a}{R} \right)^{0.341} + \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (11)$$

RESULTS AND DISCUSSION

Sensitivity of temperature-viscosity dependence to density of liquid: The analysis of viscosity is important for hydraulic calculations of fluid transport and for energy transference computation. For that, any additional accuracy in its calculation will have an important impact on the design and optimization of several industrial processes.

It is important to analyze the impact of liquids density on the viscosity-temperature dependence. This may give adequate empirical equations with better estimation accuracy.

For that, a sample of 103 experimental data on liquids viscosity over different temperature ranges at atmospheric pressure is used in this paper. It is noted that the classification of solvents into heavy liquid *versus* light liquid is commonly made according to the value of liquid density, *i.e.*, the liquid is considered as heavy if its density exceeds 1 g mL^{-1} at room temperature and atmospheric pressure and is considered as light otherwise. Thus, the classification of liquids gives 61 observations for light liquids and 42 observations for heavy liquids.

First, to test the impact of such classification on the viscosity-temperature dependence and to test if it affects significantly the distribution of the Arrhenius-Type equation parameters, we apply the Kruskal-Wallis's test [20], where the null hypothesis assumes that data from all groups are drawn from identical populations. Results are presented in Table-1.

TABLE-1
KRUSKAL-WALLIS TEST

Parameter	Liquid family	Rank sum	Chi-squared	Pr
$\ln A_s$	Light	2095.5	0.157	0.692
	Heavy	3260.5		
E_a	Light	2470.0	3.041	0.081
	Heavy	2886.0		

According to the Kruskal-Wallis test's result, the null hypothesis is rejected (at the 5% level) for both parameters. Thus, we can say that there is strong evidence that the density has statistically significant effect on the distribution of the two parameters. We expect therefore that the classification of liquids into heavy and light affect significantly the modeling of the viscosity-temperature dependence.

Following Haj-Kacem *et al.* [10], we have estimated the eqn. 5. However in our case, we have taken into consideration the effect of the density of liquids by estimating the proposed model for each group of liquids separately, with and without constant ($\alpha_1 = 0$) (Table-2).

The estimation of the eqn. 5 gives interesting results. Indeed, results with classification of liquids are different from those obtained by using the total sample. Indeed, the model's constant (α_1) becomes statistically significant if we classify the liquids. In addition, it generates a positive effect for light liquids, while for heavy liquid this effect is the opposite. This indicates that there is a need to take into consideration this

TABLE-2
ESTIMATION RESULTS OF THE eqn. 5
FOR HEAVY AND LIGHT LIQUIDS

Liquids	Coefficients		R ²	F-Fisher
	α_1	α_2		
Heavy	0	1.512073* (525.38)	0.9999	276026
	0.5451641* (-2.56)	1.621489* (38.30)	0.9734	1467
Light	0	1.521305* (866.81)	0.9999	751355
	0.4058922* (3.06)	1.43767* (52.47)	0.9790	2753
Total	0	1.517978* (906.70)	0.9999	822102
	0.0463755 (0.37)	1.50858* (59.53)	0.9723	3543.59

Notes: Values between parentheses indicate the t-statistic.

*Indicates that the coefficient is statistically significant at the 5% level.

fact when studding and modeling liquid viscosity upon temperature.

Despite the importance of this results theoretically, we suggest for practical use to consider the estimation result without constant α_1 . According to statistical point of view, the R-squared of the estimated model (5) without constant is very close to the unity and greater than those of the estimated model (5) with constant α_1 . Therefore, we deduce that the models without constants fit better the experimental data and allow better approximation accuracy.

Thus, using the new estimated values of α_2 for each group of liquids, we propose new practical equations relating the two parameters of viscosity Arrhenius-type equation, and then proposing new simplified Arrhenius-type equations depending on only one parameter instead of two with better approximation accuracy.

Thus, using the new estimated values of α_2 presented in Table-2 for each family of solvents, we suggest the improvement of the approximation accuracy of the practical equations relating the two parameters E_a and $\ln A_s$ (eqns. 6 and 7) and the simplified Arrhenius-type equations (eqns. 8 and 9) using the new coefficient values summarized in the Table-3.

TABLE-3
NEW COEFFICIENTS VALUES OF HAJ KACEM-OUERFELLI
EQUATION FOR DIFFERENT SOLVENTS POLARITY

Liquid type	λ	α_2	α_0	$1/\alpha_0$
Heavy	≈ 1	1.512073	2.9528	0.3387
Light	≈ 1	1.521305	2.9183	0.3427

To confirm that the proposed new estimated coefficients improve the approximation accuracy, we calculate the entropic factor ($\ln A_s$) and the activation energy (E_a) twice based on eqns. 6 and 7 *i.e.*, using our new coefficient values and using the old values obtained by Haj-Kacem *et al.* [10] (without classification of solvents). Table-4 summarizes the descriptive statistics of each parameter.

Descriptive statistics show clearly that the estimated values of both parameters using the new proposed practical equations are more close to the experimental values compared to those

TABLE-4
DESCRIPTIVE STATISTICS OF THE ESTIMATED *versus*
EXPERIMENTAL VALUES OF PARAMETERS

Parameter	Liquids	Method	Mean	Standard deviation
$\ln A_s$	Light	Estimated (new)	-12.579	1.907
		Estimated (old)	-12.424	1.874
		Experimental	-12.588	1.944
	Heavy	Estimated (new)	-13.214	2.559
		Estimated (old)	-13.454	2.625
		Experimental	-13.306	3.290
E_a	Light	Estimated (new)	14.430	7.668
		Estimated (old)	14.992	8.017
		Experimental	14.340	6.897
	Heavy	Estimated (new)	18.674	16.654
		Estimated (old)	19.577	17.517
		Experimental	18.874	11.707

obtained by Haj-Kacem *et al.* [10] coefficient values. This indicates that the new practical equations give better approximation accuracy of the viscosity Arrhenius-type equation parameters.

Conclusion

This paper aimed to investigate the effect of density of liquids on the modeling of viscosity temperature dependence. To achieve this purpose and using experimental data on viscosities for some pure liquids, the solvents are classified into two families as knowing heavy and light solvents.

Based on the Kruskal-Wallis statistical test, we found that there is strong evidence that the classification of liquids according to their density has statistically significant effect on the distribution of the two Arrhenius type equation parameters, the entropic factor ($\ln A_s$) and the activation energy (E_a) and thus on the modelling of the viscosity-temperature dependence.

Then, results of econometric estimation for each group of liquids separately gave interesting results. Indeed, on the one hand, statistical tests such as Kruskal-Wallis's test confirm that there is strong evidence that the density of liquids has statistically significant effect on the distribution of the Arrhenius-type equation' parameters and thus on the modeling of the viscosity-temperature dependence. This result open new perspectives for analyzing the said effect on other practical equations proposed in the literature to enhance their approximation accuracy.

On the other hand, new specific coefficient values of the equations relying the two parameters ($\ln A_s$) and (E_a) (eqns. 6 and 7) and new specific coefficient values of the simplified Arrhenius-type equation (eqn. 8 and 9) are given in this paper allowing the improvement of their approximation accuracy.

This result is important given that accuracy in the estimation of parameters and the quality of approximation is very useful in large domains of applied chemistry and engineering. For that, we expect that this study will open new interesting field of investigations such as the study of specific groups or families of organic liquids solvents and could pave the way to estimate more accurate values of the equation's parameters, when the natures of fluids are classified separately. Nevertheless, this specification may affect and restrict the boundary of the validity domain.

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