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Generalized Arrhenius Correlation for Liquid Viscosity of n-Alkanes

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Abstract: This work presents a generalized viscosity correlation for normal Alkanes (C2 to C20). The Arrhenius correlation is written in a generalized form by transforming their coefficients into fluid physical parameters of carbon number, normal boiling point temperature, critical temperature, critical pressure and accentric factor. Non parametric regression was used to develop the generalized correlation. It is validated using 245 data points covering normal Alkanes (C2 to C20). It reproduced the literature experimental data with absolute average percent deviation (AAPD) of less than 5 %. Arrhenius correlation yield similar level of accuracy. In conclusion the generalization is not made at the expense of accuracy.

Keywords: *Arrhenius ; Correlation; Normal Alkanes; Viscosity*

1. INTRODUCTION

Liquid viscosity at atmosphere pressure is generally predicted using Arrhenius correlation Eq. (1). Equation (2) is obtained from Eq. (1) by taking value of B at a viscosity of 1 mPas. Equations (3) and (4) are different modifications of Eq. (1) [1], [2].

$$\ln\mu = a + \frac{b}{T} \tag{1}$$

$$\log\mu = A\left(\frac{1}{T} - \frac{1}{B}\right) \tag{2}$$

$$\ln\mu = a + \frac{b}{T+c} \tag{3}$$

$$\ln(\mu + 0.8) = 100(0.01T)^{b} \tag{4}$$

In Eqs. (1 to 4) the viscosity (μ) is in mPas and the temperature (T) is in K. The coefficients a, b and c are obtained by fitting experimental data. These equations are widely used in the prediction of the viscosity for a wide range of fluids. However; the coefficients a, b and c are fluid specific; the values of a, b and c vary from fluid to fluid. The existing correlation are developed by parametric regression; fitting a prescribed model to data. This method will not take into account the other independent variables that characterize the fluid. Non- parametric regression such GRACE Algorithm of Breiman and Friedman [3] provides more insight to independent variables that characterize the fluid.

The objective of this work is to generalize the modified Arrhenius correlation Eq. (2) to normal Alkanes. The coefficients A and B of Eq. (2) are correlated to fluid physical parameters of critical temperature (Tc) and pressure (Pc), molecular weight (M), normal boiling point temperature (Tb) and accentric factor (ω) and carbon number (Cn) for normal Alkanes (C1 to C20) using GRACE Algorithm [3].

2. DATA BANK

The coefficients of Eq. (2) for n - Alkanes (C1 to nC20) are obtained from Reid et al. [4]. The fluid physical parameters (Tc, Pc, M, ω, Tb) are taken from Danesh [5]. The experimental values of viscosity of liquid n - Alkanes are collected from different sources. However, the bulk of the data are obtained from VDI [6], Queimada et al. [7] and Jasim [8].

3. GENERALIZATION OF VISCOSITY CORRELATION

Equation (2) is generalized by writing the coefficient A as a function of physical parameters as

$$A = f\left(C_n, M, T_b, T_c, P_c, \omega\right) \tag{5}$$

The coefficient B is treated similarly. To find the relation between the coefficients and the independent variables, non parametric regression of GRACE algorithm is used [5]. GRACE algorithm is explained in the following three steps:

1. Transformation: Fit the independent variables Cn, M, Tb, Tc, Pc, ω to each of the coefficients of Eq. (2) as

where

$$A_i(x) = \sum_i^n \beta_k x^k \tag{6}$$

where x stands for either Cn, M, T_b,T_c, P_c or ω.

2. Sum of Transformation

$$Z_i = \sum_i^n A_i(x) = f(C_n) + f(M) + f(T_b) + f(T_c) + f(P_c) + f(\omega) \tag{7}$$

3. Inverse Transformation:

$$A_i = A_i(C_n, M, T_b, T_c, P_c, \omega) = \sum_0^n \beta_i z^i \tag{8}$$

Table (1) shows the physical parameters and coefficients of Eq. (2) for n-Alkanes (C1 to nC20). Figs (1) and (2) show the dependency of coefficient A on the physical parameters (Cn; Tb; M; Tc; Pc; ω) and Figs. (3) and (4) are for coefficient B. It can be clearly noticed that there is a clear correlation between the physical parameters and coefficients. The curves are smoother for the coefficient B than that for A. It can also be noticed that [cf. Fig. (1)], the curve of A against Pc has a kink point between the critical pressure of methane and propane. The critical pressure of methane, ethane and propane are 46.99 bar, 48.72 bar and 42.48 bar respectively. Ethane has higher critical point than ethane; where trend shows otherwise. This part of the curve is inconsistent; assumes no correlation. This part is expected to yield poor correlation coefficient (r). Similar trend prevails for the relation between B and the physical parameters.

In Eqs. (6 to 8), the temperature is in K, critical pressure is in bar and molecular weight is kg/kmole. Tables (2) and (3) give the values of the constants β and correlation coefficient of Eqs. (6 and 8). It should be noted the exponent of equation 6 for normal boiling point is negative. The correlation coefficient for all fitting data is r >0.99.

4. VALIATION OF GENERALIZED VISCOSITY CORRELATION

The following statistical parameters are considered to validate the data [9], [10].

$$PD_i = \frac{X_{ex,i} - X_{cal,i}}{X_{ex,i}} 100\% \tag{9}$$

$$AAPD = \frac{1}{N} \sum |PD_i| \tag{10}$$

where (PD) is the percent deviation, AAPD is the average absolute percent deviation, Xex is the existing value, Xcal is the calculated or predicted value, N is the number of the data points and i is a dummy index. In addition, the minimum absolute percent deviation (APDmin),the maximum absolute percent deviation (APDmax) and the grand average AAPD were considered.

Table (4) shows the predicted values of the coefficients A and B of Eq. (2). As mentioned earlier and due to inconsistent in the critical pressure of Methane, Ethane and Propane the predicted values of the coefficients A and B for Methane have significant error. Against this background, Methane is considered outside the range of applicability of the generalized correlation. That is to say this work is valid for (C2 to C20). The second reason for the exclusion of methane is that, it is rarely available as liquid in range of temperature application of this model. The AAPDs for both coefficients A and B are very satisfactory as they are generally below 1.5 %; AAPDs are 1.19% and 0.54 % for A and B respectively. The APDmax is below 5 % for both A and B; AAPD are 4.38% and 2.73% for A and B respectively. Table 5 shows a summary of statistical analysis of results of comparison between experimental data and the original and generalized Arrhenius correlation. The results covered wide range of fluids nC4 to nC20. Data for C2 and C3 are rare. The total number of data point is 245.

The number of data point for each fluid ranges from 8 to 20 points. Only data that fall within the range of the correlation application is considered. The range is set by the original correlation as given in Table 5. Both original and generalized correlations produced comparable results; with a consistent grand AAPD of about 1.69 and 1.95 respectively. The error associated with generalized correlation is in the same order of the associated with original correlation. That is to say, the generalization is not made at the expense of accuracy.

5. CONCLUSIONS

The generalization of the modified Arrhenius correlation gives insight to relationship between viscosity and fluid physical parameters. The use of non parametric regression will produce more consistent correlation than parametric regression.

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BIOGRAPHY

Dr. Rabah is an associate Professor of Chemical Engineering at University of Khartoum. He received his BSc in Chemical Engineering from the University of Khartoum in 1989 and PhD (Dr.-Ing.) from the Institute of Thermodynamics at Hannover University in 2003. He was an Alexander von Humboldt fellow at the University of Helmut-Schmidt in Hamburg in 2008. He authored about 37 research papers. He supervised over 20 MSc students and more than 5 PhD students. He is a reviewer to a number of local and international journals.

Table 1: n-Alkanes physical parameters and coefficients of Eq. 2 [4], [5]

Chemical	**Formula**	**Abb.**	**Cn**	**Tb**	**M**	**Tc**	**Pc**	**ω**	**A**	**B**
Methane	CH4	C1	1	111.66	16.04	190.56	46.99	0.0115	114.14	57.60
Ethane	C2H6	C2	2	184.55	30.07	305.32	48.72	0.0995	156.60	95.57
Propane	C3H8	C3	3	231.11	44.10	369.83	42.48	0.1523	222.67	133.41
n-Butane	C4H10	nC4	4	272.65	58.12	425.12	37.96	0.2002	265.84	160.20
n-Pentane	C5H12	nC5	5	309.22	72.15	469.70	33.70	0.2515	313.66	182.48
n-Hexane	C6H14	nC6	6	341.88	86.18	507.60	30.25	0.3013	362.79	207.09
n-heptane	C7H16	nC7	7	371.58	100.20	540.20	27.40	0.3495	436.73	232.53
n-Octane	C8H18	nC8	8	398.83	114.23	568.70	24.90	0.3996	473.70	251.71
n-Nonane	C9H20	nC9	9	423.97	128.26	594.60	22.90	0.4435	525.56	272.12
n-Decane	C10H22	nC10	10	447.30	142.29	617.70	21.10	0.4923	558.61	288.37
n-Undecane	C11H24	nC11	11	469.08	156.31	639.00	19.49	0.5303	605.50	305.01
n-Dodecae	C12H26	nC12	12	489.47	170.34	658.00	18.20	0.5764	631.63	318.78
n-Tridecane	C13H28	nC13	13	508.62	184.37	675.00	16.80	0.6174	664.10	332.10
n-Tetradecane	C14H30	nC14	14	526.73	198.39	693.00	15.70	0.6430	689.85	344.21
n-Pentadecane	C15H32	nC15	15	543.83	212.42	708.00	14.80	0.6863	718.51	355.92
n-Hexadecane	C16H34	nC16	16	560.01	226.45	723.00	14.00	0.7174	738.30	366.11
n-heptadecane	C17H36	nC17	17	575.30	240.48	736.00	13.40	0.7697	757.88	375.90
n-Octadecane	C18H38	nC18	18	589.86	254.50	747.00	12.70	0.8114	777.40	385.00
n-Nonadecane	C19H40	nC19	19	603.05	268.53	758.00	12.10	0.8522	793.62	393.54
n-Eicosane	C20H42	nC20	20	616.93	282.56	768.00	11.60	0.9069	811.29	401.67

Table 2: Constants of coefficient A of Eqs. (6 and 8)

β	**Cn**	**Tb**	**M**	**Tc**	**Pc**	**ω**	**z**
1	33.4878	2055.63	1913.50	60.32	1171.50	105.16	-0.31
2	65.9461	-1.07E+06	-3178.65	-0.08	-34.69	429.39	0.17
3	-1.3589	2.14E+08	1683.03	0.00	0.28	2443.09	
4	-1.49E+10	-2.32E+02	-3569.60				
5	1435.48						
r	0.9994	0.9997	0.9988	1.00	1.00	1.00	1.00

Table 3: Constants of coefficient B of Eqs. (6 and 8)

β	**Cn**	**Tb**	**M**	**Tc**	**Pc**	**ω**	**z**
1	22.8979	11.6788	17.2083	0.50	600.89	37.81	-0.36
2	39.3627	2.80E-01	2.8377	0.20	-20.94	647.56	0.17
3	-1.5300	1.20E-03	-0.0078	0.00	0.34	-273.01	
4	2.55E-02	-1.10E-06	9.25E-06	3.15			
r	0.9998	0.9999	0.9998	1.00	1.00	1.00	1.00

Table 4: Values of A and B of Eq. (2) for n-Alkanes (C2 to C20) [1]

	Conventional			**Generalized**		
Compound	***A[1]***	***A_{cal}***	***PD***	***B1]***	***B_{cal}***	***PD***
C1	114.14	-	-	57.60	-	-
C2	156.60	156.00	0.25	95.57	97.30	-1.81
C3	223.00	213.00	435.00	133.41	129.77	2.73
nC4	265.84	268.43	-0.97	160.20	158.43	1.10
nC5	313.66	324.95	-3.60	182.48	185.32	-1.56
nC6	362.79	378.66	-4.38	207.09	209.73	-1.27
nC7	436.73	428.83	1.81	232.53	231.96	0.24
nC8	473.70	476.26	-0.54	251.71	252.67	-0.38
nC9	525.56	518.91	1.27	272.12	271.16	0.35
nC10	558.61	559.40	-0.14	288.37	288.62	-0.09
nC11	605.50	595.49	1.65	305.01	304.17	0.28
nC12	631.63	629.31	0.37	318.78	318.72	0.02
nC13	664.10	660.79	0.50	332.10	332.34	-0.07
nC14	689.85	688.21	0.24	344.21	344.19	0.01
nC15	718.51	714.53	0.55	355.92	355.67	0.07
nC16	738.30	737.91	0.05	366.11	365.93	0.05
nC17	757.88	760.32	-0.32	375.90	375.97	-0.02
nC18	777.40	780.34	-0.38	385.00	385.13	-0.03
nC19	793.62	798.58	-0.62	393.54	393.65	-0.03
nC20	811.29	816.09	-0.59	401.67	402.05	-0.09
APD_{min}			0.05			0.01
APD_{max}			4.38			2.73
AAPD			1.19			0.54

Table 5: Summary of statistical analysis of the generalized correlation

					Original			**Generalized**		
Fluid	**Data source**	**Data point**	T_{min}	T_{max}	APD_{min}	APD_{max}	*AAPD*	APD_{min}	APD_{max}	*AAPD*
C4	[6],[8]	13	195.00	256.00	0.01	10.11	3.6500	1.26	9.22	4.71
C5	[6],[8]	18	220.00	330.00	0.04	10.16	2.7200	0.16	9.47	3.79
C6	[6],[8]	18	301.00	370.00	0.01	4.56	1.2600	0.22	8.49	2.4
C7	[6],[8]	8	301.00	400.00	0.25	7.26	2.32	0.00	9.96	2.67
C8	[6],[8]	18	292.00	425.00	0.01	6.11	1.34	0.07	1.87	0.9
C9	[6],[8]	11	312.00	452.00	0.01	2.79	1.15	0.01	3.26	1.44
C10	[6],[8]	11	330.00	476.00	0.01	3.41	0.93	0.03	2.95	0.87
C11	[6],[8	12	348.00	498.00	0.02	5.92	1.24	0.01	8.69	2.01
C12	[6],[7],[8]	20	364.00	520.00	0.09	5.74	1.23	0.01	6.08	1.30
C13	[6],[7],[8]	20	380.00	540.00	0.00	5.42	1.79	0.10	5.95	2.06
C14	[6],[8]	11	394.00	560.00	0.01	4.27	1.06	0.08	4.48	1.11
C15	[6],[7],[8]	20	408.00	577.00	0.04	5.37	2.01	0.20	6.19	1.98
C16	[6],[8]	20	423.00	594.00	0.01	5.06	1.98	0.08	5.33	1.97
C17	[6],[8]	12	434.00	610.00	0.01	4.64	1.08	0.05	4.15	1.15
C18	[6],[8]	11	445.00	625.00	0.73	4.65	3.08	0.56	5.22	3.12
C19	[6],[8]	11	456.00	639.00	0.03	3.61	0.74	0.20	3.03	1.03
C20	[6],[8]	11	471.00	652.00	0.01	5.07	1.05	0.04	4.01	1.19
$\mathbf{APD_{min}}$					0	2.79	0.74	0.00	1.87	0.87
$\mathbf{APD_{max}}$					0.73	10.16	3.65	1.26	9.96	4.71
Grand AAPD		245			0.08	5.54	1.69	0.18	5.78	1.98

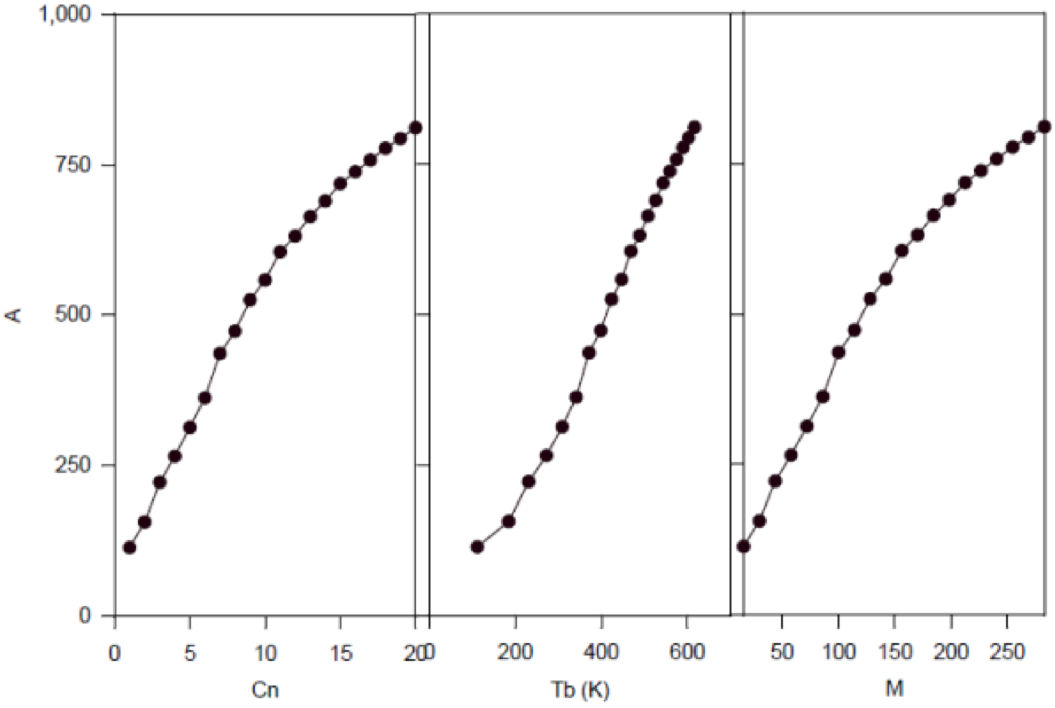

Fig.1. Dependency of the Coefficient A on C_n, T_b and M

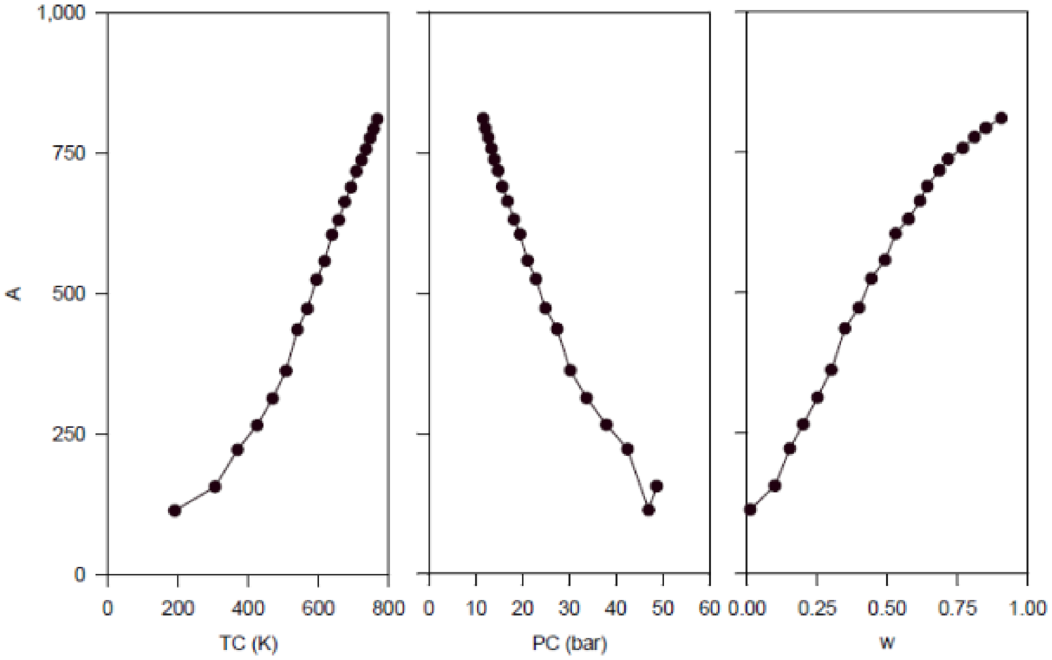

Fig.2. Dependency of the Coefficient A on T_c , P_c and W

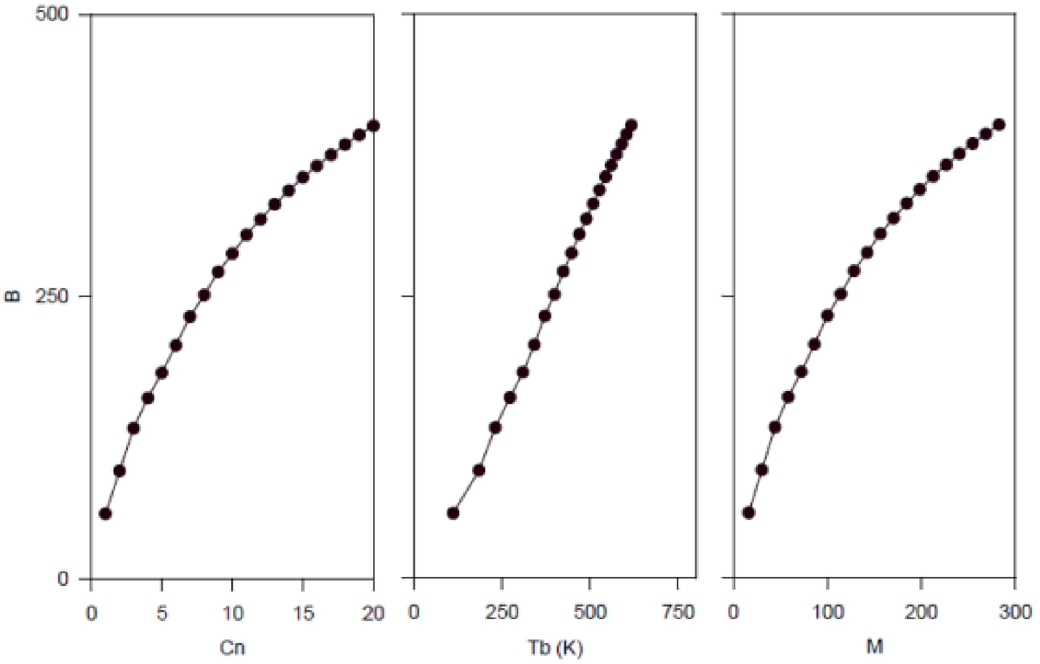

Fig.3. Dependency of the coefficient B on C_n ,T_b and M

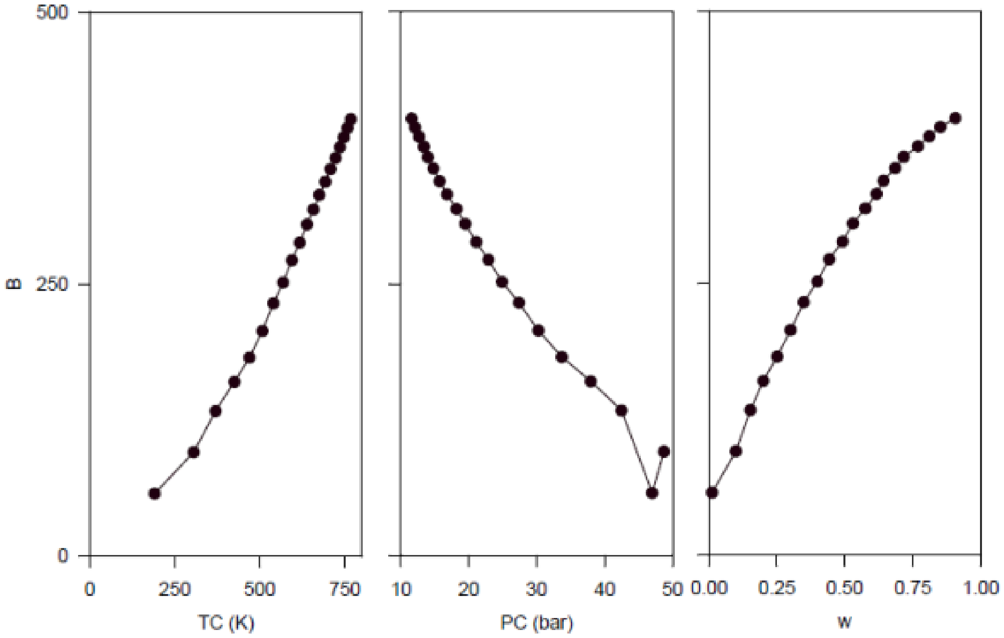

Fig.4. Dependency of the coefficient B on T_c , P_c and W