

Pressure-dependent viscosity and free volume of activation in hydrocarbons and other liquids

Piyush Kuchhal^{*1}, Gagan Anand¹, Manoj Bansal²

¹ Department of Physics, College of Engineering studies,, University of Petroleum and Energy Studies (UPES), Energy Acres, VPO Bidholi, PO Prem Nagar, Dehradun 248007, Uttarakhand, India.

² Department of Physics, Bharat Institute of Technology, Meerut (India).

*Corres.author : pkuchhal@ddn.upes.ac.in

Abstract: In the present paper, a theory based on elastic model is purposed to study the viscosity in 33 liquids including hydrocarbons and few other liquids as a function of pressure. The calculated values of viscosity in all liquids are found to be in good agreement with experimental data. The free volume activation, V_f along with the free energy of activation, E_a are also computed as a function of pressure. Further it is observed that the curvature between $\ln \eta(P, T)$ and P can be attributed to the variation of the free volume of activation associated with the flow of liquid.

Introduction

The viscosity is an important transport property of liquids because it is a structural sensitive property and may help to give an insight into the structure of liquids. In addition to that, a number of Industrial process operations take place at elevated temperature and pressure where the accurate data on the flow performance of the fluids are required to optimize them. An example is upstream oil and gas processing where the viscosity and equation of state of reservoir fluids are key properties for such calculations.

Therefore, the aim of the present paper is to develop a theory which may explain the pressure variation of viscosity in hydrocarbon and other liquids. Although the temperature dependence of viscosity is well taken and there are two well known types of viscosity – temperature behavior of liquids, namely Arrhenius and non-Arrhenius. In the higher temperature ranges the behavior usually Arrhenius but as temperature is lowered the behavior becomes non-Arrhenius. A number of empirical and semi-empirical relations are established¹⁻⁷ to explain separately both of these types of behavior but no much work has been done to explain the pressure dependence of viscosity.

Recently Kapoor & Dass⁸ has been proposed a model to explain the correct pressure dependence of viscosity but in this paper we will propose a model that can predict the pressure dependence of viscosity along with activation energy E_a & free volume of activation, V_f through the equation of state.

Theory

In general, viscosity may be considered as the integral of the interaction forces of molecules, when the interactions among molecules are very strong, they tightly hold together and are unable to slide over each other and the compound is called a solid. When energy or heat is applied up to a certain level, molecules can then slide over each other or become melted. Initially they slide over each other very slowly. If the amount of heat or temperature greatly exceeds the melting point, they move pass each other very rapidly and the liquid becomes

less viscous. The effect of temperature on the viscous flow or viscosity of liquid is discussed by eq 1 as

$$\eta(P,T) = \eta_0 e^{-\frac{E_a(P,T)}{RT}} \quad (1)$$

Where η_0 is a pre-exponential constant and E_a is the free energy of activation for flow.

As aforementioned, molecular motion or flowing of liquids depends on the interactive force among molecule; it is speculated that, the molecular interactive force will increase as the pressure is increased. Thus, it is proposed that eq 1 will also be applied to predict the pressure-dependence of liquid.

$$\eta(P,T) = \eta_0 e^{-\frac{E_a(P,T)}{RT}} \quad (2)$$

where, η_0 is a constant. Similarly at pressure P_0

$$\eta(P_0,T) = \eta_0 e^{-\frac{E_a(P_0,T)}{RT}} \quad (3)$$

Combining eqs 2 & 3 gives

$$\ln \left[\frac{\eta(P,T)}{\eta(P_0,T)} \right] = \frac{E_a(P_0,T)}{RT} \left[1 - \frac{E_a(P,T)}{E_a(P_0,T)} \right] \quad (4)$$

The basic idea of this model is the same as that of free volume model⁴ and shove model⁶, namely the activation energy is elastic energy. This elastic energy is located in the surroundings of the rearranging molecules. The fact that the surroundings liquid behave as a solid during flow event. Thus the value of $E_a(P,T)$ may be expressed as

$$E_a(P,T) = C(P,T) V(P,T) B_T(P,T) \quad (5)$$

where B_T & V are the isothermal bulk modulus and volume of the liquid, respectively. $C(P,T)$ is dimension less pressure-dependent parameters. The idea expressed in eq. (5) is not new. Earlier Dass *et al*^{9,10} have used this type of the idea to explain the pressure dependence of self-diffusion in solids. Similarly eq. (5) can also be expressed at pressure P_0 and temperature T as

$$E_a(P_0,T) = C(P_0,T) V(P_0,T) B_T(P_0,T) \quad (6)$$

Combining eqs 5 and 6 on the assumption that

$$C(P,T) = C(P_0,T) [1 - \alpha(P - P_0)] \quad (7)$$

gives

$$E_a(P,T) = E_a(P_0,T) \left[\frac{V(P,T)}{V(P_0,T)} \right] \left[\frac{B_T(P,T)}{B_T(P_0,T)} \right] \quad (8)$$

Here α is an adjustable parameter. It is shown theoretically that $C(P,T)$ is really a pressure dependent quantity¹⁰ and not a pressure independent parameter.

The free activation volume $V_f(P,T) = \left. \frac{dE_a(P,T)}{dP} \right|_T$ is

$$V_f(P,T) = E_a(P,T) \left[\frac{-\alpha}{1 - \alpha(P - P_0)} + \frac{1}{B_T(P,T)} \left[\left. \frac{dB_T(P,T)}{dp} \right|_T - 1 \right] \right] \quad (9)$$

Now to compute the values of E_a & V_f , we need the relations for $\frac{V(P,T)}{V(P_0,T)}$, $\frac{B_T(P,T)}{B_T(P_0,T)}$ and $\left. \frac{dB_T(P,T)}{dp} \right|_T$.

In the present paper, we use the relations given by Kuchhal and Dass¹¹.

$$\frac{V}{V_0} = 1 - \frac{2}{\beta} \ln \left[1 + \frac{\beta}{3B_{T0}} (P - P_0) \right]^{3/2} \quad (10)$$

Where $\beta = 3B_{T0}' + 2$

$$B_T = B_{T0} \left(\frac{V}{V_0} \right)^{2/3} \exp \left[-\frac{\beta}{2} \left\{ \left(\frac{V}{V_0} \right)^{2/3} - 1 \right\} \right] \quad (11)$$

$$B'_T = \frac{1}{3} \left[\beta \left(\frac{V}{V_0} \right)^{2/3} - 2 \right] \quad (12)$$

In eqs 10 and 12, B_{T0} and B'_{T0} are the bulk modulus and its first derivative at $p=p_0$ respectively.

Calculations and Discussions

The present model has been applied to hydrocarbons and other liquids reported in Table 1. Although the values of EOS parameters in eqs 11 and 12 are available in the literature for some of the liquids, but in this study the values of B_{T0} and B'_{T0} are obtained by least square fittings by using the experimental density in respective liquids and reported in Table 1. The RMSE is also reported to indicate the goodness of fit. The fitted values of B_{T0} and B'_{T0} are compared with the data of others wherever they are available.

Eqs 10 and 11 are substituted in eq 4 to obtain the values of adjustable parameters α & E_a (P_0, T) in each liquid. The values obtained by least-square fitting are reported in Table 1. Once all the parameters become known, the values of viscosity, $\ln \eta(P,T)$ are computed as a function of pressure and plotted in Figure 1 for selected liquids where either the curvature is large or very small. A good agreement exists between the calculated and experimental data as is clear from RMSE and Figure 1. Actually the agreement is within $\pm 10\%$ which seems not to be unusual taking into account the experimental errors involved in the measurement of viscosity.

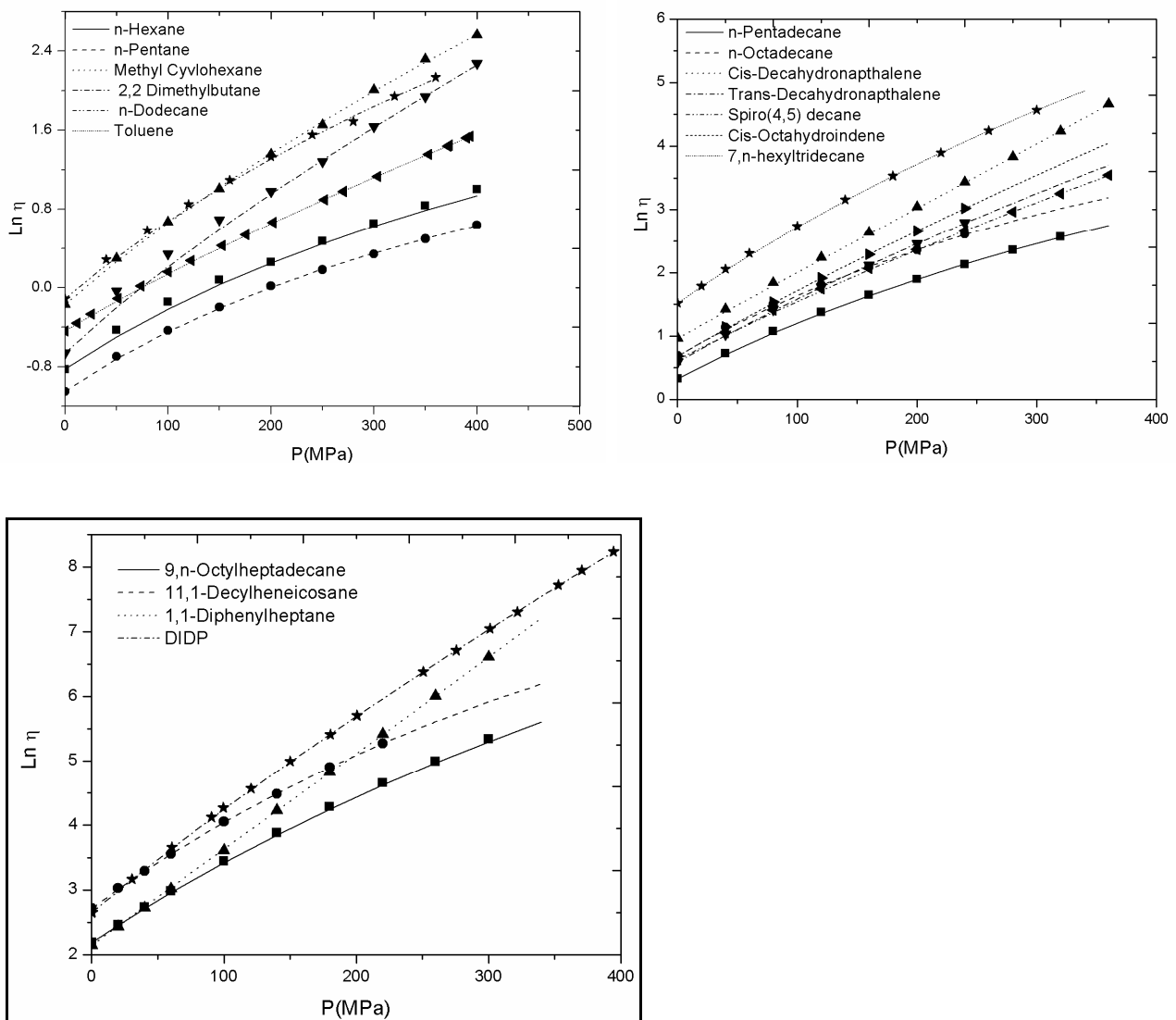


Fig.1: Variation of $\ln \eta(P,T)$ with pressure in different liquids. Solid symbols representing the experimental data while solid line is representing the present work.

Table-1 Viscosity Calculation parameters in different liquids

Sr No	Liquid	η_0 centipose	T_A (K)	P MPa	$E_a(0, T_A)$ J/mole	α	$B_T(P_0, T_A)$ MPa	$B_T'(P_0, T_A)$	RMSE (V/V ₀)	RMSE (η)	Ref for V/V ₀ & η
1	Toluene	0.5557	298.15	0.1- 393.5	2335.9	1.57e-04	1103.2 1089[20]	9.28	1.65e-04	0.019	12
2	n-Hexane	0.285	303.15	0.1-40	1568.6	4.58e-04	608.1 560.5[20]	9.27	8.57e-04	0.029	13
3	n-Octane	0.487	303.15	0.1-40	2210.4	2.02e-04	832.1 710.22[20]	9.02	5.29e-04	0.073	13
4	n- Pentane	0.216	303.15	0.1-140	1469.0	5.41e-04	500.8	8.53	1.05e-03	0.014	13
5	Cyclopentane	0.390	303.15	0.1-380	2034.7	5.88e-04	705.6	9.18	1.01e-03	0.057	13
6	Methyl Cyclohexane	0.641	303.15	0.1-40	2985.8	2.33e-04	939.4	9.07	8.45e-04	0.118	13
7	2,2-Dimethyl butane	0.330	303.15	0.1-40	1606.7	1.59e-04	527.7	10.12	6.76e-04	0.107	13
8	[OMIM]BF ₄	341	298.15	0.1-224	4958.4	3.35e-04	2004.4	14.60	4.35e-05	1.02	14
9	[BMIM]PF ₆	273	298.15	0.1-250	5116.8	2.92e-05	2235.2	16.12	9.80e-05	6.02	15
10	DIDP Sample B	13.2	338.15	0.1-394.4	5419.2	1.23e-04	1229.8	12.41	6.79e-04	9.51	16
11	n-dodecane	0.63	352.59	0.1-360	2356.1	4.37e-04	732.9	10.34	4.66e-04	0.118	17&19
12	n-pentadecane	1.01	352.59	0.1-320	3225.9	4.94e-04	860.6	9.89	2.56e-04	0.063	17&19
13	n-octadecane	1.48	352.59	0.1-320	3898.5	6.39e-04	932.2	9.91	8.87e-05	0.085	17&19
14	Cis-Decahydronapthalene	2.31	310.93	0.1-360	4192.1	-2.28e-04	1416.7	10.46	1.68e-04	0.405	17&19
15	Trans-Decahydronapthalene	1.546	310.93	0.1-240	4094.1	2.33e-04	1268.1	10.43	2.15e-04	0.049	17&19
16	Spiro(4,5) decane	1.619	310.93	0.1-360	3759.5	1.52e-04	1284.9	10.37	2.06e-04	0.149	17&19
17	Spiro(5,5) undecane	2.212	310.93	0.1-240	6187.3	-9.13e-05	1568.1	8.47	3.08e-04	0.096	17&19
18	Cis-Octahydroindene	1.723	310.93	0.1-240	5409.9	9.04e-05	1388.1	8.85	2.09e-04	0.063	17&19
19	Trans-Octahydroindene	1.225	310.93	0.1-360	3437.1	-8.298e-05	1166.8	9.79	2.09e-04	0.104	17&19
20	7-n-Hexyltridecane	3.53	310.93	0.1-300	4678.2	4.01e-04	1117.5	10.17	2.67e-04	0.253	18&19
21	9-n-octylheptadecane	7.06	310.93	0.1-300	5589.6	4.17e-04	1257.7	9.95	1.76e-04	0.742	18&19
22	11-n-Decylheneicosane	12.1	310.93	0.1-300	6719.5	4.57e-04	1353.8	9.52	1.74e-03	1.713	18&19
23	13-n-Dodecylhexacosane	9.98	334.15	0.1-300	5528.4	4.51e-04	1221.5	10.05	7.05e-04	0.573	18&19
24	1,1-Diphenylethane	2.85	310.93	0.1-340	3447.2	-1.65e-03	1762.42	9.75	1.21e-03	0.643	18&19

25	1,1-Diphenylheptane	7.98	310.93	0.1-300	7653.3	-3.12e-04	1648.7	9.17	1.15e-03	0.834	18&19
26	1,1-Diophenyltetradecane	7.91	333.15	0.1-260	5894.5	1.86e-04	1368.5	10.97	1.77e-04	0.533	18&19
27	9(2-cyclohexylethyl)heptadecane	12.1	310.93	0.1-340	7255.4	3.15e-04	1425.6	10.04	9.23e-05	3.111	18&19
28	9(2-Phenylethyl)heptadecane	7.92	310.93	0.1-340	6648.1	2.81e-04	1493.3	9.81	2.15e-04	1.429	18&19
29	1,2,3,4,5,6,7,8,13,14,15,16-Dodecahydrochrysene	5.00	388.15	0.1-140	133.2	-0.268	1608.1	10.80	5.75e-05	26.55	18&19
30	Perhydrochrysene	10.4	333.15	0.1-180	136.1	-0.347	1862.3	9.57	1.96e-04	16.32	18&19
31	1,1-Di(alpha-decalyl)hendecane	17.3	372.04	0.1-140	8458.3	-8.82e-04	1293.0	11.34	3.93e-04	14.27	18&19
32	1-alpha-Decalylpentadecane	3.55	372.04	0.1-340	5044.8	2.82e-04	1168.7	10.69	1.13e-04	0.387	18&19
33	1-alpha-naphthylpentadecane	341	372.04	0.1-260	4879.4	1.85e-04	1286.7	10.21	1.26e-04	0.0313	18&19

The combination of eqs 8-12 give the values of free energy of activation and free volume of activation at different pressures. The computed results for both parameters, $E_a(P,T)$ and $V_f(P,T)$ are plotted in Figure 2 and Figure 3, respectively. To the best of our knowledge no experimental or theoretical values of free energy of activation and free volume of activation for these liquids have so far been reported for comparison. But, it is clear from Figure 2 that V_f decreases with the increase in pressure in most of the liquids except in some liquids where it is increasing with pressure. The increase in V_f with pressure is not unusual because in such liquids the curvature of $\ln \eta(P,T)$ Vs P curves is just opposite than other liquids where V_f is decreasing with pressure. In some liquids where curvature is small the V_f is almost constant with pressure. These observations reveal that the free volume of activation may be responsible for the curvature in the plot of $\ln \eta(P,T)$ Vs pressure.

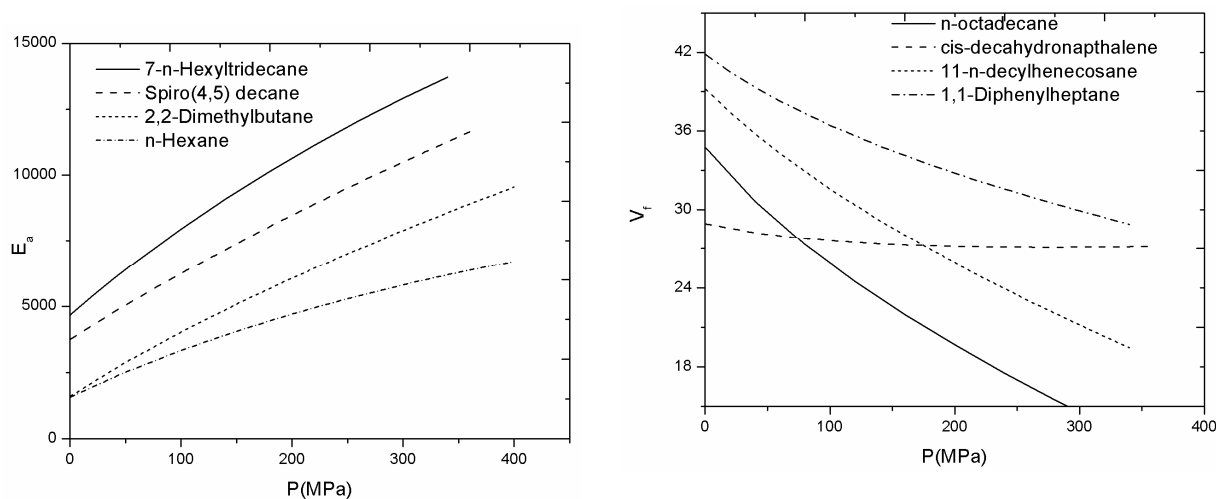


Fig.2: Variation of free energy of activation in different liquids

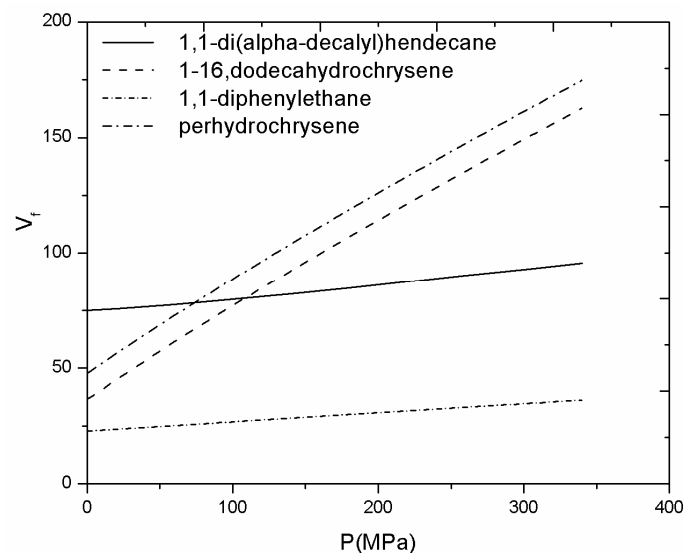


Fig.3: Variation of free volume of activation in different liquids

Conclusion

In conclusion, it can be said that the EOS is successful in describing the viscosity, free activation volume and energy as a function of pressure in case of hydrocarbons and other liquids as well. The present model may provide a basis on which a more profound and basic theory of viscosity of the

hydrocarbons may be developed. Moreover, at present it provides a convenient means for representing the experimental data including interpolations and extrapolations.

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