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PRESSURE-DEPENDENT VISCOSITY AND FREE VOLUME IN LIQUIDS THROUGH MELTING TEMPERATURE APPROACH

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ABSTARCT

In the present paper, a model based on the melting temperature approach is purposed to study the viscosity in three liquids viz Benzene, n-Dodecane, and n-Octadecaneas a function of pressure. The calculated values of viscosity in all three liquids are found to be in good agreement with experimental data. The free volume activation, V_f*is 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 associated with the flow of liquid.*

Keywords : Free Volume Activation, Liquids, Melting Temperature, Viscosity, Pressure.

I. INTRODUCTION

The aim of the present paper is to develop a theory which may explain the pressure variation of viscosityin 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 Arrheniusbut as temperature is lowered the behavior becomes non-Arrhenius. A number of empirical and semi-empirical relations are established[1-7] to explain separately both of these types of behavior but no much work has been done to explain the pressure dependence of viscosity.

Recently Kuchhal& Dass[8]has been proposed a model to explain the correct pressure dependence of self-diffusion through melting temperature approach.The aim of present work is to extend the work of Kuchhal &Dass to predict the pressure dependence of viscosity of liquids along with free volume of liquids,V_f.

II.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 (1) as

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

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

In most of the liquids, the melting temperature is found to increase with increasing pressure. On the other hand, the viscosity is found to decrease with rising pressure, indicating that activation energy must decrease with increasing pressure. Therefore it is worthwhile to consider the linear relationship between activation energy and melting temperature which is also used by other workers in past [9-10].

$$E_a(P,T) = A(T)R\,T_m - E(T) \quad (2)$$

Where T_m is the melting temperature at pressure P, T is the ambient temperature at which η(P,T) data are available as a function of temperature. A(T) and E(T) are pressure independent but temperature dependent parameters and R is the universal gas constant.

Equation (1) and (2) can be used to define the viscosity as

$$\ln \eta(P,T) - \ln \eta_0 = -\left[\frac{A(T)T_m}{T}\right] + \left[\frac{E(T)}{RT}\right] \quad (3)$$

Differentiating of equation (4) with respect to T_m/T keeping T constant gives

$$[\partial \ln \eta(P,T)/\,\partial(T_m/T)]_T = A(T) \quad (4)$$

Therefore the physical significance of A(T) is that its represent the slope of straight line obtained by plotting ln η(P,T) versus T_m/T for a liquid at a given temperature T.

Further, at P=0 and temperature T, equation (3) can also be written aS

$$\ln \eta(0,T) - \ln \eta_0 = -\left[\frac{A(T)T_0}{T}\right] + \left[\frac{E(T)}{RT}\right] \quad (5)$$

Eqs(3) and (5) can be combined to give

$$\eta(P,T) = \eta(0,T)\exp[-A(T)(T_m - T_0)/T] \quad (6)$$

The melting temperature as a function of pressure can be obtained from Simon's relation [11] given as

$$T_m = T_0[1 + \beta P]^C \tag{7}$$

Where T_m and T_0 are the melting temperatures at pressure P and P=0, respectively.
Differentiating (2) with respect to pressure gives the free volume $V_f(P,T)$ as

$$[\partial E_a(P,T)/\partial P]_T = V_f = A(T)R\frac{dT_m}{dP} \tag{8}$$

Eq(8) can alternatively written as

$$V_f(P,T) = A(T)RT_0C\beta(1 + \beta P)^{C-1} \tag{9}$$

with the help of (7).

III.CALCULATIONS AND DISCUSSIONS

The present model is applied in the case of Benzene [12], n-Dodecane [13] and n-Octadecane [13]. While the parameters involved in the (7) are taken from Babb [14].
Eqs(6) and (7) are used to obtain the values of adjustable parameterA(T) in each liquid. The values obtained by least-square fitting along with other relevant parameters are reported in "Table 1". Once all the parameters become known, the values of viscosity, lnη(P,T) are computed as a function of pressure and plotted in "Figs.1-3" for all liquids. A very good agreement exits between the calculated and experimental data as is clear from reduced chi-square and "Figs.1-3". Actually the agreement is within ± 0.5% which seems not to be unusual taking into account the experimental errors involved in the measurement of viscosity.
The combinationof Eqs (2) & (9) give the values of free energyand free volume at different pressures. The computed result for free volume$V_f(P,T)$ in all liquids are plotted in "Fig.4". To the best of our knowledge no experimental or theoretical values of free volume forthese liquids have so far been reported for comparison. But, it is clear from "Fig.4" that $V_f$decreases with the increase in pressure in all three liquids. 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.

Table-1 :Values of melting constants A(T), β and C along with other relevant parameters

Liquid	T_0 (K)	T (K)	A(T)	β (MPa^{-1})	C	Reduced Chi-Square
Benzene	278.8	303.15	-8.55	0.00278	0.38	2.30

n-Dodecane	263.65	298.15	-13.36	0.00282	0.327	0.00297
n-Octadecane	300.95	323.15	-15.17	0.00289	0.295	0.004

IV. FIGURES AND TABLES

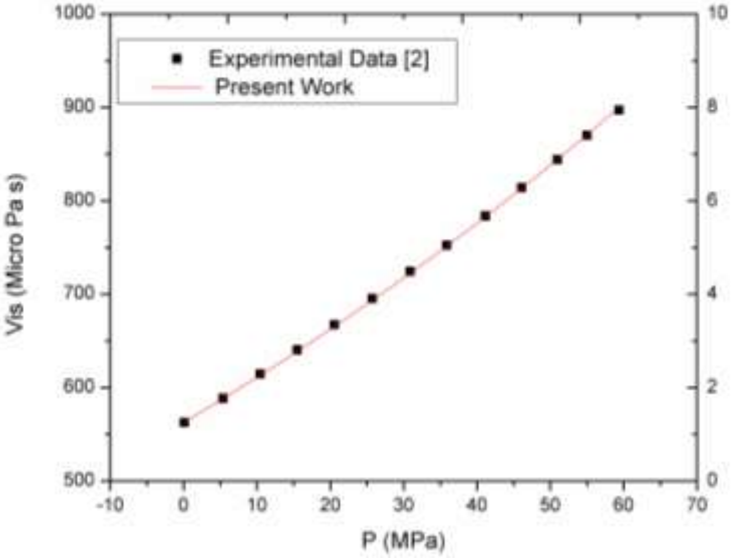

Fig.1: lnη(P,T) against P in case of Benzene at 303.15K

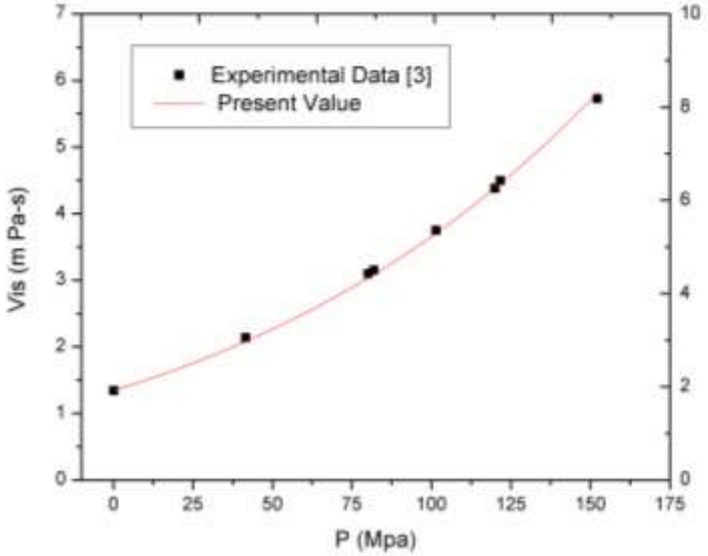

Fig.2: lnη(P,T) against P in case of n-Dodecane at 298.15.15K

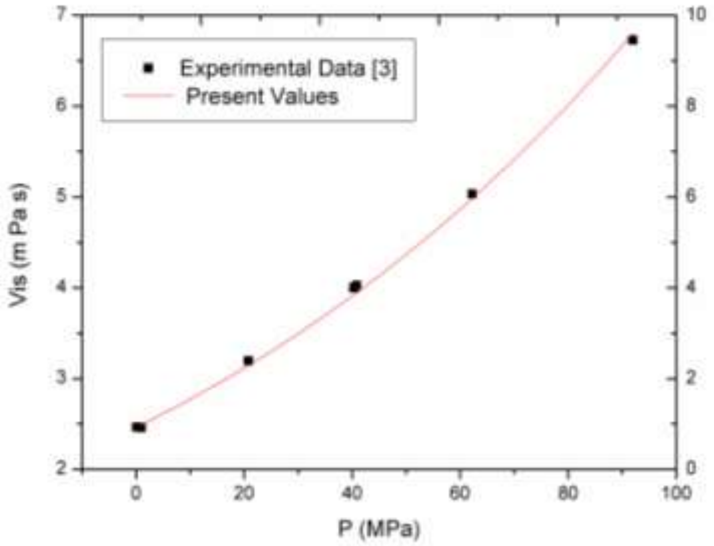

Fig.3: lnη(P,T) against P in case of n-Octadecane at 323.15K

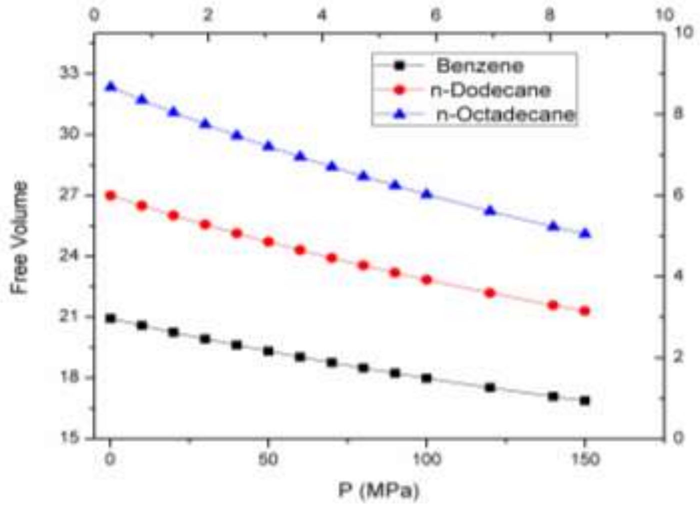

Fig.4: $V_f(P,T)$ against P in case of Benzene, n-dodecane and n-octadecane

V.CONCLUSION

In conclusion, it can be said that the melting temperature approach is successful in describing the viscosity, and free volume as a function of pressure in case of all three liquids. The present model may provide a basis on which a more profound and basic theory of viscosity of the liquid may be developed. Moreover, at present it provides a convenient means for representing the experimental data including interpolations and extrapolations.

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