

Effective Debye temperature and specific heat ratio in liquid methane and pentane

J. D. PANDEY AND H. C. PANDEY

Department of Chemistry, University of Allahabad, Allahabad 2110032

(Received 6 May 1975, revised 11 August 1975)

Assuming quasi-crystalline structure of liquids, effective Debye temperatures for the liquids methane and pentane are calculated as a function of temperature, and pressure. Debye temperatures for liquid methane are further used in computing the values of specific heat ratio (γ) with the help of certain parameters given in standard literature. The values so obtained are in fair agreement with those published earlier. The variation of θ with temperature and pressure is as usual.

Neutron scattering technique (Singwi *et al.* 1960, Egelstaff 1965) and other evidences (Hughes *et al.* 1959, Hughes *et al.* 1960) are available in literature which support the quasi-crystalline behaviour of liquids. The structure of liquids can be denoted by the term quasi-crystalline in the sense that they display a certain degree of local order of the same type as that of the corresponding crystals. The study of dynamics of atomic motion of liquids plays very important role in understanding the solid like behaviour of liquids. Unfortunately no successful theory is available in literature to explain such dynamical behaviour of liquids. On the basis of quasi-crystalline model, Joshi (1961) and other evaluated the Debye temperature of water at a particular temperature which is in good agreement with the values given by Singwi *et al.* (1960). Such type of calculations have recently been extended (Kor *et al.* 1974, Kor *et al.* 1973) to other liquids (water, ethanol, methanol, toluene, hexane) assuming the atomic motions in these liquids as similar to those of solids.

In all the above mentioned methods of calculating the values of Debye temperature, the ultrasonic absorption and shear viscosity data were employed. The present paper deals with the evaluation of effective Debye temperature of liquid pentane and liquid methane as a function of temperature and pressure assuming the quasi-crystalline model for these liquids. Here we have modified the usual procedure for calculating the Debye temperature so as to avoid the use of ultrasonic absorption data.

The previous workers calculated the values of θ (Kor *et al.* 1974, Kor *et al.* 1973, Joshi 1961) by using the parameter A given below

$$A = \left(\frac{K_{T,\infty}}{K_{T,0}} \right) \left(\frac{\eta_v}{\eta_s} \right) \left(\frac{\tau_s}{\tau_v} \right), \quad \dots (1)$$

where all the terms have their usual significance, further the ratio $\frac{K_{T,\infty}}{K_{T,\gamma}}$ can be simplified by using the well known relation

$$\frac{1}{K_{T,\infty}} = \frac{1}{K_{T,0}} - \frac{1}{K_{T,\gamma}} \quad \dots (2)$$

And simplified relation can be written as,

$$\left(\frac{K_{T,\infty}}{K_{T,\gamma}} \right) = \left(\frac{K_{T,\infty}}{K_{T,0}} \right) - 1 = \frac{1}{\gamma} - 1 = \frac{1-\gamma}{\gamma}, \quad \dots (3)$$

where γ is the heat capacities ratio

According to Litovitz & Davin (1965)

$$\frac{\tau_s}{\tau_v} = \frac{4}{3} \eta_s \beta_{T,0} \frac{K_{T,\gamma}}{\eta_v} \quad \dots (4)$$

We have from eqs (2) and (4)

$$\left(\frac{\tau_s}{\tau_v} \right) = \frac{4}{3} \left(\frac{\eta_s}{\eta_v} \right) \frac{K_{T,\infty}}{K_{T,\infty} - K_{T,0}} \quad \dots (5)$$

which reduces to

$$\left(\frac{\tau_s}{\tau_v} \right) \left(\frac{\eta_v}{\eta_s} \right) = \frac{4}{3} \frac{1}{1-\gamma}$$

Combining eqs (6), (3) and (1), we get

$$A = + \frac{4}{3} \frac{1}{\gamma} \quad \dots (7)$$

From this relation, the Poisson's ratio is given by (Joshi 1961)

$$\sigma = \frac{2-\gamma}{4+\gamma} \quad (8)$$

Thus we need only γ , ρ and $\beta_{T,\infty}$ for calculating the effective Debye temperature θ

Results and Discussion

Data on ultrasonic measurements in liquid methane (Singer 1969) and liquid pentane (Richardson 1957) have been utilised for calculating the values of θ at different temperatures and pressures. In case of liquid methane, the values of θ were calculated at constant pressure with variable temperature, at constant temperature with variable pressure and at constant density with variable temperature and pressure while in liquid pentane, only pressure is varied. Further, θ values for liquid methane are utilised in computing γ values with the help of

standard literature (American Institute of Physics Handbook 1963) The results of above calculations are presented in tables 1 and 2

Table 1 Temperature dependance of Debye temperature θ for liquid methane at constant pressure 1.68 kg/cm²

Temperature in °K	Density in gm/cc.	θ in °K	γ_{cal}	γ_{*rel}
112	0.421	94.15	1.85	1.76
105	0.438	108.98	1.83	1.72
94	0.450	110.18	1.84	1.69

*Singer J. R. 1969 *J. Chem. Phys.* 51, 4729

Pressure dependance of Debye temperature θ for liquid methane at constant temperature (112.0 ± 1) °K

Pressure in kg/cm ²	Density in gm/cc	θ in °K	γ_{cal}	γ_{*rel}
1.68	0.421	94.15	1.80	1.76
30.8	0.424	98.90	1.88	1.75
62.5	0.427	101.59	1.85	1.73
89.0	0.430	104.90	1.83	1.74

*Singer J. R. 1969 *J. Chem. Phys.* 51, 4729

Temperature and pressure dependance of Debye temperature for liquid methane at constant density 0.420 gm/cc

Pressure in kg/cm ²	Temperature in °K	θ in °K	γ_{cal}	γ_{*rel}
2.4	113.0	91.80	1.90	1.78
7.9	113.6	91.80	1.89	1.70
14.1	114.0	91.80	1.89	1.80
27.0	115.0	91.80	1.89	1.81
52.0	117.0	93.77	1.88	1.83

*Singer J. R. 1969 *J. Chem. Phys.* 51, 4729.

As seen from tables, Debye temperature θ increases with pressure for both liquids while decreases with temperature for liquid methane. It is interesting to

Table 2. Pressure dependence of θ for liquid pentane at 15°C

Pressure in kg/cm ²	θ in °K
00.0	33.27
07.0	34.33
14.1	35.78
21.1	36.16
28.1	36.39
35.2	38.49
42.2	39.40
49.2	40.17
56.2	42.18

note that θ did not change at constant density while the temperature and pressure were varied. The variation of θ and its magnitude for both the liquids are very similar to those of non-associated liquids (Kor *et al* 1974) which was expected also γ values for liquid which were derived from corresponding Debye temperatures on assumption that liquid behaves as solid, are very close to those (Singer 1969) published previously and hence support the quasi crystalline model for liquids. Due to lack of C_p values, no comparison could be made for liquid pentane. Moreover, similarities regarding the magnitude and nature of variation of θ for liquid pentane with non-associated liquids are sufficient basis for the prediction of its values. Thus the results so obtained can be summarised by stating that the Debye temperature in liquids may have more or less the same meaning as in solids for the interaction of the order of 10^{-13} sec.

Authors are thankful to S.C.S.I.R. (U.P.) for providing the financial assistance.

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