Estimation of effective Debye temperature of some liquids and their Isotopes by acoustic method

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Abstract: Acoustic methods have been applied to estimate the effective Debye temperature (θ_D) of pure liquids and their isotopes. The theoretical approach employed earlier has been completely modified and a new approach has been suggested. Five pure liquids and their isotopes have been undertaken for computing the values of effective Debye temperature using the present approach. The necessary experimental data needed have been taken from literature.

Key words: Debye temperature, ultrasonic velocity, temperature.

1. Introduction

The structure of a liquid can be denoted by the term quasi-crystalline in the sense that liquid displays a certain degree of local order of the same type as that of corresponding crystal. The study of dynamics of atomic motion of a liquid plays very important role in understanding the solid like behavior of liquids. So the name effective Debye temperature has been given. On the basis of quasi-crystalline structure and other experimental evidences, a number of workers[1-9] evaluated the effective Debye temperature of various liquids as a function of temperature and pressure. These workers utilized ultrasonic absorption, velocity, density and compressibility data of liquid for the estimation of effective Debye temperature. In the subsequent development[8] the theoretical approach has been modified to enable the calculation of Debye temperature from sound velocity, density, compressibility and heat capacities ratio data. Qualitatively, the concept of effective Debye temperature has been introduced to few binary liquid mixtures in the year 1979[10]. Since then the study of effective Debye temperature has not been progressively done. In the present work, we are introducing a fresh approach to study the effective Debye temperature of pure liquids and their isotopes.

Previously, Debye temperature of liquids has been computed on the basis of approximate equivalence of β_T and β_a, just as in the case of solids. Here we have assumed $\beta_a \neq \beta_T$, as α has considerable values in liquids but not in solids. So $\gamma \neq 1$.

2. Theoretical

The expression for Debye temperature (θ_D) for a solid is given by

$$\theta_D = \frac{h}{k}\left[\left(\frac{9N}{4\pi V}\right)\Big/\left(\frac{1}{C_l^3}+\frac{2}{C_t^3}\right)\right]^{1/3} \qquad (1)$$

where *h*, *k* *N* and V are Planck's constant, Boltzmann's constant, Avogadro number and molar volume respectively.

here

$$\left(\frac{1}{C_l^{3}}+\frac{2}{C_t^{3}}\right)=\left(\rho\beta_a\right)^{3/2}\left[\left\{\frac{(1+\sigma)}{3(1-\sigma)}\right\}^{3/2}+2\left\{\frac{2(1+\sigma)}{3(1-2\sigma)}\right\}^{3/2}\right] \qquad (2)$$

In the above expression β_a can be written as follows

$$\beta_a=\beta_T-\frac{TV\alpha^2}{C_p} \qquad (3)$$

where α, C_p, β_T are expansivity, the specific heat at constant pressure and the isothermal compressibility respectively. For the solid, α is very small, so the second term is neglected for solids, and,

$$\beta_a \approx \beta_T \qquad (4)$$

Equation (4) has been used only for the solids, but recently some workers[11] used this assumption in calculating Debye temperature of liquids and liquid mixtures. In the case of liquids, α has considerable value so here we have modified above approach by assuming $\beta_a \neq \beta_T$ and β_a has been calculated from the relation

$$\beta_a=(\rho_{mix}u^2{}_{mix})^{-1} \qquad (5)$$

Poisson ratio has been calculated as

$$\sigma=\frac{3A-2}{6A+2} \qquad (6)$$

where

$$A=\left(\frac{K_{T,\infty}}{G_{T,\infty}}\right)=\left(\frac{K_{T,\infty}}{K_{T,r}}\right)\left(\frac{\eta_v}{\eta_s}\right)\left(\frac{\tau_s}{\tau_v}\right) \qquad (7)$$

and using the relation given by Davis and Litovitz[12] we can write

$$\left(\frac{K_{T,\infty}}{K_{T,r}}\right)\left(\frac{\eta_v}{\eta_s}\right)\left(\frac{\tau_s}{\tau_v}\right)=\frac{4}{3\gamma}$$

$$A=\frac{4}{3\gamma} \qquad (8)$$

where γ is defined as the ratio of isothermal compressibility to adiabatic compressibility given as

$$\gamma=\frac{\beta_T}{\beta_a} \qquad (9)$$

where β_T is calculated from recently proposed relation[13]

$$\beta_T=\frac{1.71\times10^{-3}}{u^2.T^{4/9}.\rho^{4/3}} \qquad (10)$$

3. Results and Discussion

The values of Debye temperature of pure liquids viz. H_2O, C_6H_6, C_6H_{12}, CH_3OH, C_2H_5OH and their isotopes D_2O, C_6D_6, C_6D_{12}, CH_3OD, C_2H_5OD have been calculated at four different temperatures 293.15, 303.15, 313.15 and 323.15 K with the help of above procedures. The required data needed for the computations has been taken from literature[14]. Calculated values of Debye temperature of pure liquids are given in Table-1. Equations (1) to (10) have been used to obtain the values of Debye temperature of liquids and their isotopes under consideration.

A close perusal of table-1 shows that Debye temperature of pure liquids and their respective isotopes are decreasing with increase in temperature except H_2O and its isotope. This also indicates that Debye temperature decreases for heavy molecules. This is due to increase in density and decrease in ultrasonic velocity of heavy molecules.

4. References

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Table1: Debye Temperature of pure liquids and its isotopes at different temperatures

H_2O	ρ (gm/cm^3)	u(m/s)	y	V	θ_D
293.15	0.9991	1483	1.37	18.03	157.20
303.15	0.9983	1511	1.35	18.05	159.36
313.15	0.9967	1531	1.33	18.08	160.65
323.15	0.9940	1545	1.31	18.12	161.28
D_2O					
293.15	1.0524	1386	1.35	19.03	143.48
303.15	1.0509	1413	1.33	19.06	145.51
313.15	1.0489	1434	1.31	19.10	146.92
323.15	1.0471	1448	1.29	19.13	147.62
C_6H_6					
293.15	0.9376	1327	1.40	83.31	85.05
303.15	0.9311	1280	1.38	83.89	81.51
313.15	0.9256	1232	1.36	84.39	77.98
323.15	0.9199	1184	1.35	84.91	74.49
C_6D_6					
293.15	0.9711	1246	1.38	86.65	78.51
303.15	0.9653	1201	1.37	87.17	75.21
313.15	0.9594	1156	1.35	87.71	71.95
323.15	0.9541	1111	1.33	88.20	68.75
C_6H_{12}					
293.15	0.8823	1280	1.43	95.38	78.94
303.15	0.8772	1230	1.41	95.94	75.39
313.15	0.8713	1180	1.39	96.59	71.87
323.15	0.8661	1130	1.38	97.17	68.42
C_6D_{12}					
293.15	0.9435	1153	1.40	102.01	69.02
303.15	0.9377	1110	1.38	102.64	66.03
313.15	0.9312	1068	1.36	103.36	63.14
323.15	0.9255	1026	1.35	104.00	60.29
CH_3OH					
293.15	0.8895	1122	1.42	36.02	95.64
303.15	0.8848	1089	1.41	36.21	92.27
313.15	0.8788	1057	1.39	36.46	89.00
323.15	0.8735	1024	1.37	36.68	85.71
CH_3OD					
293.15	0.8990	1103	1.42	36.76	93.28
303.15	0.8943	1071	1.40	36.96	90.02
313.15	0.8882	1040	1.38	37.21	86.87
323.15	0.8824	1008	1.37	37.45	83.69

C_2H_5OH

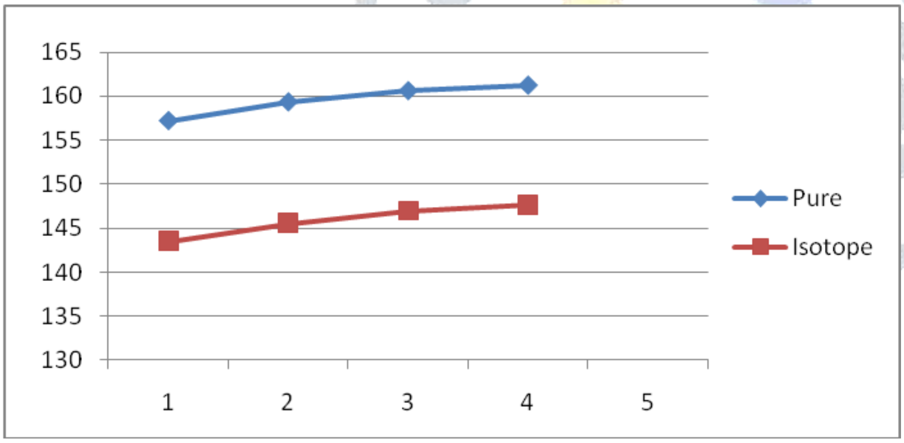
293.15	0.8890	1167	1.42	51.82	88.13
303.15	0.8835	1133	1.41	52.15	85.02
313.15	0.8788	1098	1.39	52.42	81.91
323.15	0.8734	1064	1.37	52.75	78.90

C_2H_5OD

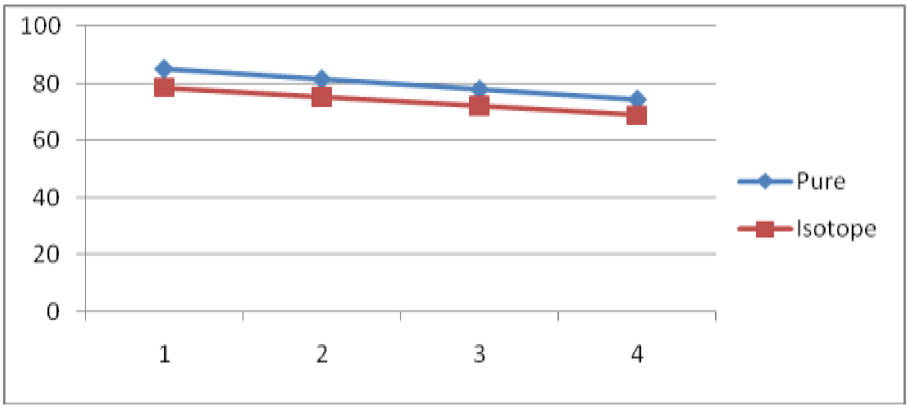
293.15	0.8979	1145	1.42	52.43	86.03
303.15	0.8930	1111	1.40	52.72	82.97
313.15	0.8877	1077	1.38	53.03	79.94
323.15	0.8822	1043	1.37	53.36	76.96

Graph: Variation of Debye Temperatures of pure liquids and its isotopes.

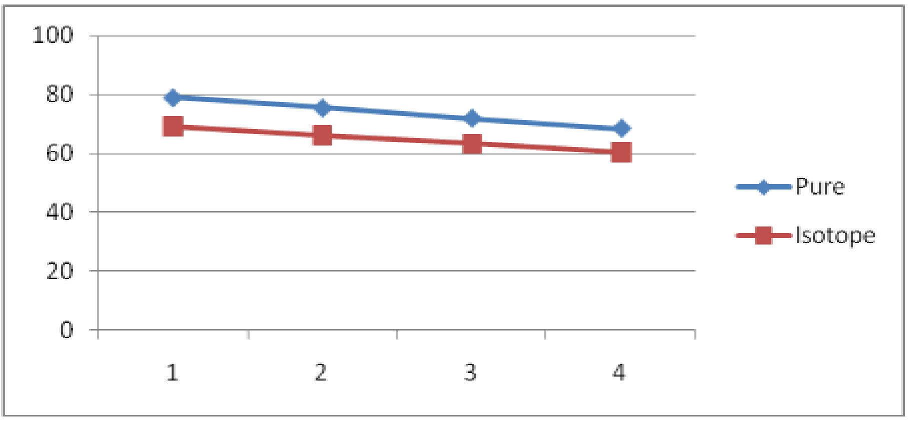
H_2O & D_2O



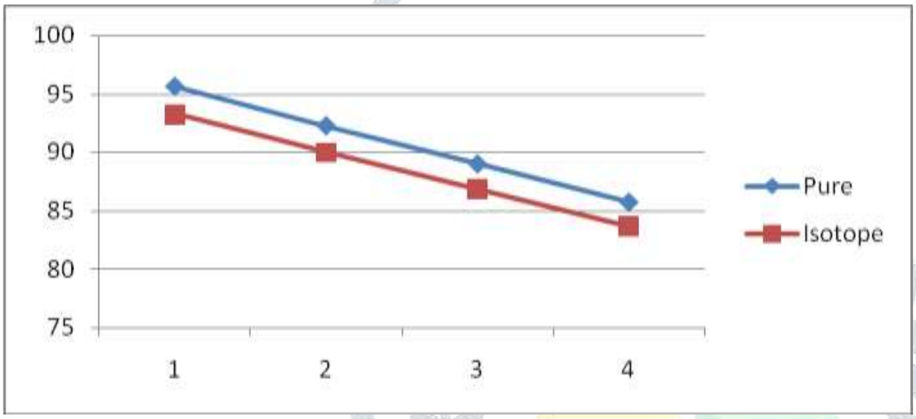
C_6H_6 & C_6D_6



C_6H_{12} & C_6D_{12}



CH_3OH & CH_3OD



C_2H_5OH & C_2H_5OD