Thermal Properties of Some Organic Liquids Using Ultrasonic Velocity Measurements

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Abstract: Debye temperature and thermal relaxation time has been calculated in normal and boiling temperature. Using thermal relaxation time, the heat of fusion has been calculated for nineteen organic liquids and the results throw light on the method of calculating heat of fusion.

Keyword: Debye temperature, Heat of fusion, Ultrasonic velocity, Thermal properties

Introduction

Physical, chemical and thermo acoustical parameters of liquids, liquid mixtures, polar and non polar solutions and liquefied gases are very important for industrial applications. Ultrasonic velocity measurements has been carried out to bring out physical, chemical and thermal properties of liquids, liquid mixtures, polar and non polar solutions using its allied parameters like density, viscosity, surface tension *etc.*, Ultrasonic measurement is one of the easiest method to calculate the properties of liquids like compressibility, internal pressure and so on¹⁻⁷.

In the present work, an attempt is made to calculate Debye temperature and relaxation time of liquid at normal and boiling temperature. Using relaxation time, heat and fusion has been calculated for the 19 organic liquids such as methanol, acetic acid, ethylene glycol, chloroform, heptane, octane, phenol, acetone, pentane, ethanol, benzene, toluene, glycerin, butanol, pentanol, methyl propanol, hexanol, propanol and heptanol.

Theory and calculations

Ultrasonic velocity and applied parameters are used to calculate Debye temperature as⁸

$$\Theta = (h/k_B) \{ [9N/4\pi V] / [(1/C_l^3) + (2/C_t^3)] \}^{1/3} \quad (1)$$

Where,

h is the Planck's constant in Js,

k_B is the Boltzmann's constant in J/K,

N is the Avagadro number in kg/mol,

V is the volume of the liquid m³.

$$\frac{1}{C_1^3} = \left[\frac{1 + \sigma}{3(1 - 2\sigma)} \right]^{3/2} (\rho\beta_T)^{3/2} \quad (2)$$

$$\frac{1}{C_1^2} = \left[\frac{2(2 + \sigma)}{3(1 - 2\sigma)} \right]^{3/2} (\rho\beta_T)^{3/2} \quad (3)$$

Where,

C_l is velocity of longitudinal waves in m/s,

C_t is velocity of transverse waves in m/s,

ρ is the density of liquid in kg/m³

$$\sigma = (3A - 2)/(6A + 2) \quad (4)$$

$$A = 4/3 (1/\nu) \quad (5)$$

$$\beta_T = \beta_s = 1/u^2 \rho \quad (6)$$

Where,

β_T is adiabatic compressibility of liquid in m²/N

β_s is the isothermal compressibility of liquid in m²/N

ν is ratio of specific heats in m²/N

Relaxation time is related with Debye temperature as⁹

$$\tau = (h/2\pi\theta_D K_\beta) \quad (7)$$

Heat of fusion of liquid can be found as follows⁹

$$H = \ln(\tau_B/\tau_R) \times KT \quad (8)$$

Where,

τ_B is relaxation time at boiling temperature in sec

τ_R is relaxation time at normal temperature in sec

Sound velocity at boiling temperature is calculated using the relation¹⁰⁻¹¹

$$C_{\text{gas}} = C_{\text{liquid}} (V_f/V)^{1/3} \quad (9)$$

Where,

V is the molar volume of the liquids in m³

V_f is the free volume in m³

Results and Discussion

Table 1 gives the values of sound velocities and densities of normal temperature and boiling temperature for 19 organic liquids. By treating liquids on polycrystalline solid⁹, the thermal properties such as relaxation time and Debye temperature of organic liquids are calculated at normal temperature and boiling temperature and presented in Table 2. From Debye's relaxation time, the heat of fusion has been calculated and presented in Table 2.

In all system, densities and velocities at boiling temperature are less than the normal temperature. This is due to free space created between the molecules/atoms by temperature. This is conformed by the value of Debye temperature. The value of debye temperature at boiling point is less than those at normal temperature that is the disorder increases at boiling temperature.

Table 1. Velocity and density of some organic liquids at normal and boiling temperature

Liquid	C* normal temp, m/s	C* boiling temp, m/s	ρ normal temp, kg/m ³	ρ boiling temp, kg/m ³
Methanol	1143	0995.378	0791	0476.450
Ethylene glycol	1644	1175.881	1113	0814.821
Heptane	1138	1079.860	0684	0368.840
Glycerine	1904	1178.289	1261	1019.516
Octane	1171	1102.414	0703	383.283
Phenol	1274	0445.229	0107	0102.618
Acetic acid	1584	1419.274	1049	0610.129
Acetone	1190	1146.275	0780	0411.918
Chloroform	0995	0898.606	1483	0853.941
Pentane	1044	1012.982	0626	0327.147
Ethanol	1144	0976.823	0789	0486.276
Benzene	1295	1180.358	0868	0494.181
Toulene	1275	1130.660	0867	0510.767
Glycerine	1904	1177.848	1262	1019.516
Butanol	1228	1573.510	0809	0261.420
Pentanol	1256	1586.372	0814	0270.015
Methyl propanol	1110	1418.030	0802	0259.020
Heptanol	1305	1608.090	0818	0284.912
Propanol	1190	1543.360	0803	0252.407
Hexanol	1283	1598.780	0813	0276.686

(* Ref : 12)

Table 2. Thermal properties of some organic liquids

Liquid	Relaxation time $\times 10^{-13}$ s		Debye temperature, K		Heat of fusion, (Cal/g)
	Normal temp	Boiling temp	Normal temp	Boiling temp	
Methanol	0.8094	1.1005	94.45	69.47	26.86
Acetic acid	0.1654	0.8754	116.76	87.33	72.37(44.07)
Ethylene glycol	0.6259	0.9722	122.14	78.64	27.72
Chloroform	1.1679	1.5530	65.46	49.23	6.62(19.01)
Heptane	1.1264	1.6513	61.34	47.33	8.85
Octane	1.2541	1.6321	60.94	46.82	7.65
Phenol	2.0256	5.8901	37.75	12.97	42.93
Acetone	1.0054	1.2910	76.19	59.37	10.11
Pentane	1.2550	1.6060	60.91	47.59	8.75
Ethanol	1.0950	1.2580	83.72	60.77	8.70
Benzene	0.9315	1.2323	82.07	61.99	10.55(30.01)
Toulene	1.0000	1.3448	76.43	56.85	10.27
Glycerine	0.5911	1.0256	129.33	74.54	19.05
Butanol	0.9875	1.1250	77.41	67.95	4.24
Pentanol	1.0222	1.1695	74.79	65.37	5.22
Methyl propanol	1.0965	1.2495	69.72	61.18	5.58
Heptanol	1.0770	1.2423	70.98	61.54	4.58
Propanol	0.9538	1.0817	80.15	70.67	4.70
Hexanol	1.0770	1.2081	72.70	63.28	4.87

Calculated heat of fusion from Debye's relaxation time throws light on the author's idea. Literature value available is presented in parenthesis¹². The deviation may be explained after elaborate study.

Conclusions

From this study, ultrasonic velocity at boiling temperature, values of thermal properties like Debye's temperature and relaxation time at normal and boiling temperature are expected range, that is Debye temperature at normal temperature > boiling temperature and relaxation time at normal temperature < boiling temperature. Another thermal property, heat of fusion from thermal relaxation time is a fresh attempt for organic liquids. Values of heat of fusion support new approach.

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