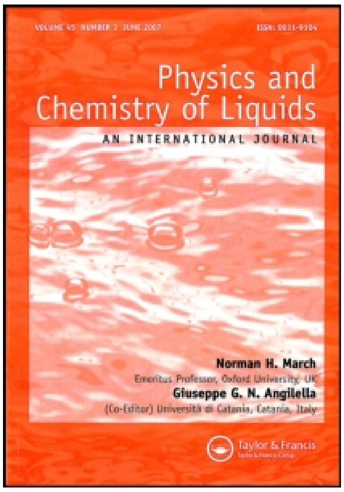
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

The Study of Molecular Interactions in Liquids Using Temperature Variation of Ultrasonic Velocity

G. K. Johri[a]; J. Singh[b]; M. Johri[a]; Saumya[b]
[a] Department of Physics and Electronics, D.A-V. College, Kanpur, India [b] Department of Chemistry, P.P.N. College, Kanpur, India

To cite this Article Johri, G. K. , Singh, J. , Johri, M. and Saumya(2000) 'The Study of Molecular Interactions in Liquids Using Temperature Variation of Ultrasonic Velocity', Physics and Chemistry of Liquids, 38: 5, 509 — 519
To link to this Article: DOI: 10.1080/00319100008030299
URL: http://dx.doi.org/10.1080/00319100008030299

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phys. Chem. Liq., 2000, Vol. 38, pp. 509–519
Reprints available directly from the publisher
Photocopying permitted by license only

© 2000 OPA (Overseas Publishers Association) N.V.
Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Downloaded At: 07:59 28 January 2011

THE STUDY OF MOLECULAR INTERACTIONS IN LIQUIDS USING TEMPERATURE VARIATION OF ULTRASONIC VELOCITY

G. K. JOHRI[a,]*, J. SINGH[b], M. JOHRI[a] and SAUMYA[b]

[a] *Department of Physics and Electronics, D.A-V. College, Kanpur 208 001, India;* [b] *Department of Chemistry, P.P.N. College, Kanpur 208 001, India*

(Received 23 June 1999)

The associative behaviour of organic liquids resulting from molecular interactions using ultrasonic velocity data taken from the literature is reported and a classification of these liquids is done as associative categories I and II along with the normal one. This work is fruitful to understand chemico-physical properties of organic liquids and departures from the normal characteristics.

Keywords: Molecular interaction; interaction potential; ultrasonic velocity

1. INTRODUCTION

The molecular interactions in liquids can not be described by the assumption of simple, potential functions. Johri *et al.* [1] have studied the physical association and chemical bonding within the frame work of Hirschfelder [2] treatment on inter molecular forces. They have formulated an effective potential for non-polar liquids using the continuum dielectric model with the Lernard-Jones (LJ) and the Kihara (K) potential. In the past an extensive of the Anderson's model [3] has been introduced to describe the dielectric relaxation process of pure hydrogen bonded liquids [4, 5]. The ultrasonic technique [6] is one

---

*Corresponding author.

of the good ones. When the propagation of low amplitude ultrasonic wave in a liquid is considered it merely perturbs its physical chemical equilibria. The ultrasonic velocity as a function of temperature determine the overall response of the medium and the nature of the interaction between the molecules of the liquid.

The purpose of this paper is to report a classification of organic liquids and to compute the nature and degree of association as a result of intermolecular forces in different types of organic liquids. The organic compounds chosen are alkanes, alkenes, alkyne derivative, alkyl phenyl ketone, alkyl-*p*-xylyl-ketone, alcohols, 4-R-acetophinon, 4-R-propiophinon, 4-R-isobutysophenon, 4-R-pivalophenon, alkyl acetate and 35 other liquids with almost normal behaviour. The experimental data of ultrasonic velocity as a function of temperature for these liquids have been taken from the literature [7].

Downloaded At: 07:59 28 January 2011

2. THEORETICAL DETAILS AND CALCULATIONS

The ultrasonic velocity (c) could be written as a function of density (ρ), molecular weight (M), temperature (T), potential parameter (σ), depth of the potential (ε), range of the potential (r), core parameter (l), ionization potential (I), polarizability (α) and shape of molecule (sp)

$$c = f(\rho, M, T, \sigma, \varepsilon, r, l, I, \alpha, sp) \tag{1}$$

For normal liquids, where only cohesive forces are important one can reduce the above Eq. (1) to the following form within reasonable limits of approximation.

$$c = c^* f(\rho, M, T) \tag{2}$$

where c^* is the proportionality constant. This Eq. (2) could be written as

$$c = c^* f(\rho) f(M) f(T) \tag{3}$$

Using dimensional method of analysis Eq. (3) could be reduced to

$$\frac{\Delta C}{\Delta T} = M^{-1/2} C^* f(\rho) \tag{4}$$

Downloaded At: 07:59 28 January 2011

or

$$M^{1/2}\frac{\Delta C}{\Delta T} = C^{*}f(\rho) \tag{5}$$

This theoretical expression empirically derived is general and new and it may be realistic provided the value of $c^{*}f(\rho)$ may be experimentally or theoretically derived. Comparing Eq. (5) with that of Lagemann [8] equation where in the R.H.S. has been experimentally obtained one gets following equation

$$M^{1/2}\frac{\Delta C}{\Delta T} = 39\,g^{1/2}\,\mathrm{ms}^{-1}\,\mathrm{deg}^{-1} \tag{6}$$

Equation (6) may be reasonable only for the normal liquids for which attractive interactions between the molecules play a minor role and that they are in the nature of cohesive forces called London dispersive attractive forces. The Lagemann factor [6] was derived from the study of the substance $C_6H_5{-}X$ (X = H, F, Cl, Br, and I) at 500 kHz. They observed non-linear characteristics for the variation of temperature of the ultrasonic velocity with molecular weight.

We define the degree of association as the fractional change in the Lagemman factor and its percentage is given by

$$\text{Percent degree of association} = \frac{\Delta L}{L} \times 100\% \tag{7}$$

$$\text{where } \Delta L = \left| M^{1/2}\frac{\Delta C}{\Delta T} \right|_{\text{Ass. Liq}} - \left[M^{1/2}\frac{\Delta C}{\Delta T} \right]_{\text{Norm. lq.}} \tag{8}$$

$$\Delta L = \left| L_{\text{Ass. Liq}} \right| - 39 \tag{9}$$

The associativeness in liquids may thus be measured as deviations from normal behaviour. The degree of association values depending upon the inter-molecular attractive interaction, temperature *etc*. The Eq. (7) provides quantitative measure of association. It is pertinent to mention that the liquids which behave as associated at room temperature may behave like normal at higher temperature when thermal energy breaks molecular links.

Downloaded At: 07:59 28 January 2011

3. RESULTS AND DISCUSSIONS

Table I includes values of the molecular weight, $M^{1/2}(\Delta C/\Delta T)$ and percent degree of association for thirty organic liquids. The plot of temperature variation of ultrasonic velocity against molecular weight is given in Figure 1 for the substances listed in Table I as well as for various radicals in 4-R-acetophenon, 4-R-propiophenon, 4-R-pivalophenon and alkylacetate listed in Table II. The Figure 2 illustrates the variation

TABLE I The values of molecular weight $M^{1/2}(\Delta C/\Delta T)$ and percent degree of association for organic liquids with almost normal behaviour

Sl. no.	*Substance*	*M*	$M^{1/2}(\Delta C/\Delta T)$ $g^{1/2}ms^{-1}deg^{-1}$	$\Delta L/L \times 100\%$
1	Methyl Acetate	74	39.57	1.46
2	Benzene	78	39.57	1.46
3	*n*-hexane	84	38.50	−1.28
4	Hexane	86	40.80	4.62
5	1,4-dioxane	88	40.53	3.92
6	Aniline	93	39.06	0.15
7	*n*-heptane	98	39.60	1.53
8	Fluoro-benzene	95.9	40.84	4.72
9	*o*-xylol	106.0	39.12	0.31
10	*n*-tolulidine	107	37.24	−4.51
11	*n*-octane	112	41.80	7.18
12	Chlorobenzene	112.5	39.45	1.15
13	*n*-heptanol	116	39.85	2.18
14	Methylphenylketone	120	40.53	3.92
15	*o*-nitrophenol	123	39.93	2.38
16	Nitrobenzene	123	39.93	2.38
17	Guajacol	124	41.20	5.64
18	*o*-Chlorotolual	126.5	40.49	3.82
19	*m*-Chlorotolual	126.5	40.83	4.69
20	*p*-Chlorotolual	126.5	40.49	3.82
21	*o*-Chloroaniline	127.5	39.52	3.82
22	*m*-Chloroaniline	127.5	38.39	−1.56
23	*m*-Octanol	130	41.05	5.26
24	Tetraline	132	41.59	6.64
25	*o*-nitrotolual	137	39.80	2.05
26	Propyl Phenyl Ketone	148	40.15	2.95
27	Carbon Tetrachloride	154	39.21	0.54
28	Bromobenzene	156.9	39.08	+0.21
29	Fluoren	166	39.94	2.41
30	Diphenyleneoxide	168	39.53	1.36
31	*O*-Bromotolual	170.9	40.13	2.94
32	*p*-Bromotolual	170.9	39.61	1.31
33	α-nitro napthaline	173	40.77	4.54
34	Benzophenon	182	40.47	3.77
35	Iodobenzene	203.9	38.55	−1.41

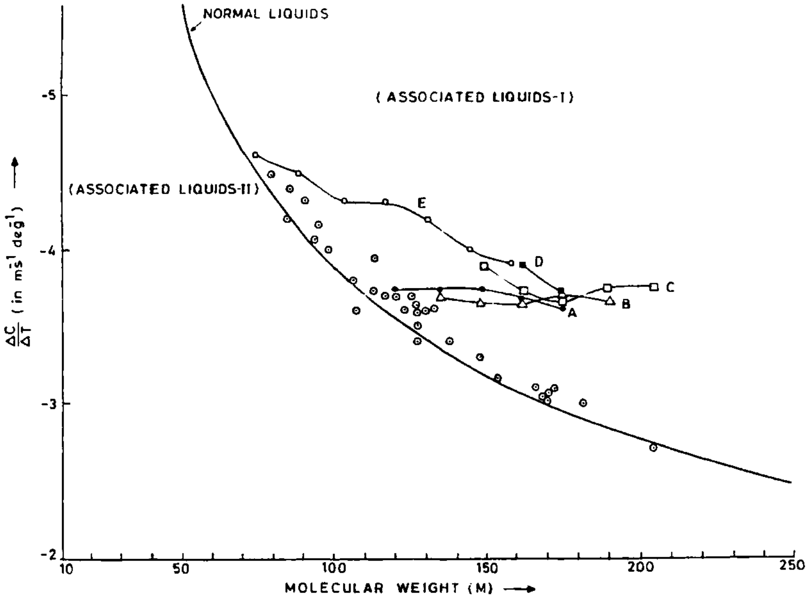


FIGURE 1 Temperature variation of ultrasonic velocity $(\Delta C/\Delta T)$ *versus* molecular weight for the normal liquids (Tab. I). A: 4-R Acetophenon; B: 4-R Propiothenon; C: 4-R Isobutyrophenon; D: 4-R-Pivalophenon; E: Alkyl acetatic with different radical (R) (Tab. II).

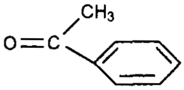
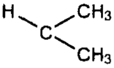
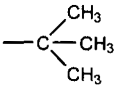
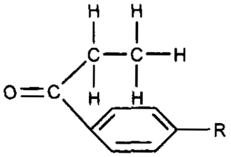
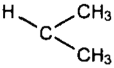
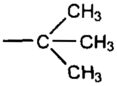
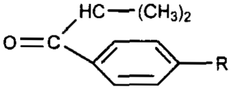
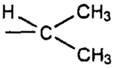
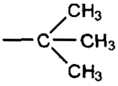
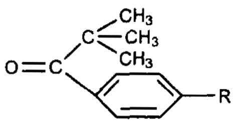
of $(\Delta C/\Delta T)$ *versus* molecular weight for substances listed in Table III called as associated liquids – I and those listed in Table IV, categorized as associated liquids – II. Table V lists the values of $M^{1/2}(\Delta C/\Delta T)$ and percent degree of association for alkanes (C_nH_{2n}; $n = 5-10, 12, 14, 16$), alkenes (C_nH_{2n}; $n = 5-11, 13, 15$), alkyne (C_nH_{2n-2}; $n = 5-8, 10, 12$), alkyl acetate ($C_nH_{2n}O_2$; $n = 3$ to 9), alkyl-phenyl-ketone ($C_{n+p}H_{n+2p}O$; $n = 8, p = 0$ to 7), alkyl-*p*-xylyl-ketone (C_nH_{n+2p}; $n = 10, p = 1$ to 29) and alcohols ($C_nH_{2n+2}O$; $n = 1$ to $8, 10$).

The plot of $(\Delta C/\Delta T)$ *versus* M for these systems listed in Table V and also for alcohols are illustrated in Figure 3.

We have presented a new way for classifying the organic liquids in three categories namely normal, associated – I and II liquids. There is significant divergence of both. These categories of association from normal liquids. The location of point in the variation of $(\Delta C/\Delta T)$ *versus* M following on the concavity side is designated under category as category – I and that on convexity side as category – II. Most of those

Downloaded At: 07:59 28 January 2011

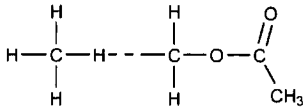
TABLE II The values of $M^{1/2}(\Delta C/\Delta T)$ and percent degree of association for 4-R-acetaphenon, 4-R-Propiophenon, 4-R-Isobutyrophenon, and 4-R-Pivalophenon with different radicals (R) and alkyl acetates

Substance	*Radical* *R*	$|M^{1/2}(\Delta C/\Delta T)|$ $g^{1/2} ms^{-1} deg^{-1}$	$L/\Delta L$ 100%
A. 4-R-acetophenon	H	40.53	3.92
$C_{n+p}H_{n+2p}O\begin{pmatrix} n = 8 \text{ to } 12 \\ p = 0 \text{ to } 4 \end{pmatrix}$	$—CH_3$	43.41	11.31
	$—C_2H_5$	44.40	13.85
		47.09	20.74
		47.76	22.46
B. 4-R-propiophenon	H	42.83	9.82
$C_{n+p}H_{n+2p}O\begin{pmatrix} n = 8 \text{ to } 12 \\ p = 1 \text{ to } 5 \end{pmatrix}$	$—CH_3$	45.62	16.97
	$—C_2H_5$	46.46	19.13
		48.95	25.51
		50.31	29.00
C. 4-R-Isobutyrophenon	H	47.45	21.67
$C_{n+p}H_{n+2p}O\begin{pmatrix} n = 8 \text{ to } 12 \\ p = 2 \text{ to } 6 \end{pmatrix}$	$—CH_3$	47.09	20.74
	$—C_2H_5$	48.42	24.15
		51.69	32.54
		53.56	37.33
D. 4-R-Pivalophenon	H	49.64	27.28
$C_{n+p}H_{n+2p}O\begin{pmatrix} n = 8 \\ p = 3, 4 \end{pmatrix}$	CH_3	49.09	25.87
			

Downloaded At: 07:59 28 January 2011

Downloaded At: 07:59 28 January 2011

TABLE II (Continued)

Substance	*Radical* *R*	$\lvert M^{1/2}(\Delta C/\Delta T)\rvert$ $g^{1/2}\,ms^{-1}\,deg^{-1}$	$L/\Delta L$ 100%
E. Alkylacetate	Methyl acetate	39.57	1.46
	Ethyl acetate	42.21	8.23
$C_nH_{2n}O_2(n = 3)$	*n*-propyl acetate	43.43	11.36
	*n*-Butyl acetate	46.31	18.74
	n-Amyl acetate	47.89	22.79
	n-Hexyl acetate	48.00	23.08
	n-Heptyl acetate	49.02	25.69

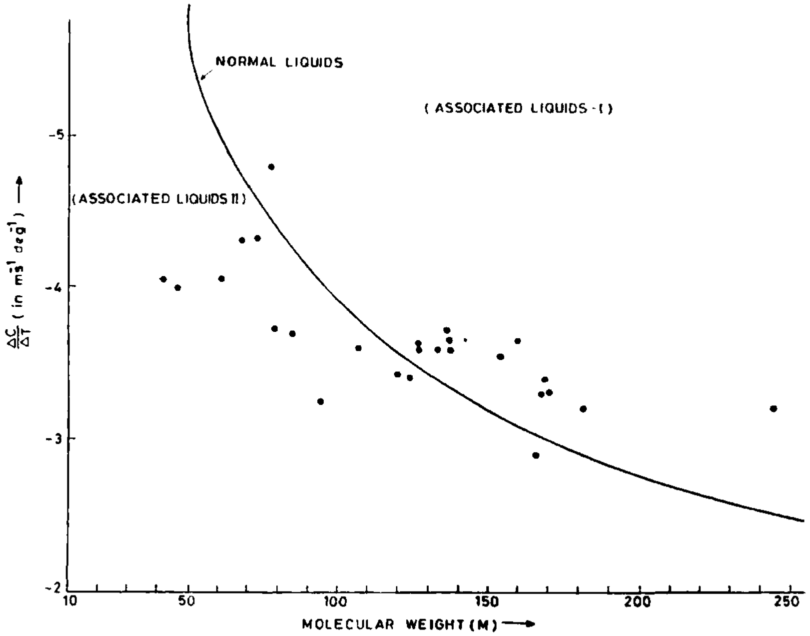


FIGURE 2 Temperature variation of ultrasonic velocity ($\Delta C/\Delta T$) *versus* molecular weight for organic liquids (Tabs. III, IV).

chemicals whose divergence from the curve of variation of ($\Delta C/\Delta T$) *versus* M is less than 5 percent have been interpretted as normal liquids.

An examination of Figure 1 reveals that chemical grouped as A, B, C, D have ($\Delta C/\Delta T$) variation less than above 8 percent for $\Delta M = 80$. However, group E possesses variation of ($\Delta C/\Delta T$) about 19.5 percent

TABLE III The molecular weight $M^{1/2}(\Delta C/\Delta T)$ and degree of association for associated liquids – I

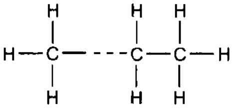
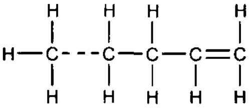
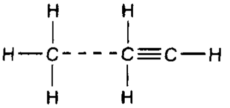
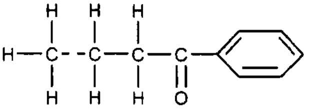
Associated liquids – I *substance*	*M*	$\lvert M^{1/2}(\Delta C/\Delta T)\rvert$ $g^{1/2} ms^{-1} deg^{-1}$	$(\Delta L/L)$ 100%
n-Heptanol	116	39.85	2.18
n-Octanol	130	41.04	5.23
n-Decanol	158	46.51	19.26
Benzene	78	42.22	8.26
o-Chlorotolual	126.5	40.83	4.69
m-Chlorotolual	126.5	40.83	4.69
p-Chlorotolual	126.5	40.49	1.26
o-Nitrotolual	137	42.72	9.52
m-Nitrotolual	137	42.14	8.05
n-Octane	114	45.06	11.05
dibenzene	182	43.17	15.57
phenyl cyclohexane	160	46.17	18.38
diphenylamine	169	44.20	13.33
diphenyl ether	170	43.16	10.67
diphenyl methane	168	43.55	11.67
tri-phenyl methane	244	49.99	28.18

TABLE IV The molecular weight $M^{1/2}(\Delta C/\Delta T)$ and degree of association for associated liquids – II

Associated liquids – II *substance*	*M*	$\lvert M^{1/2}(\Delta C/\Delta T)\rvert$ $g^{1/2} ms^{-1} deg^{-1}$	$(\Delta L/L)$ 100%
Methanol	32	18.67	−52.13
Ethanol	46	23.06	−40.87
n-propanol	60	28.66	−26.51
n-butanol	74	34.41	−11.77
n-pentanol	88	32.83	−15.82
n-hexanol	102	35.35	−9.36
1-pentene	72	35.46	–
Nitro methane	61	31.63	−18.90
Chloroform	119.5	37.50	−3.85
Methyl Chloride	84	35.74	−8.36
Tetrachloroethylene	166	37.36	−4.21
Glycerine	92	17.94	−54.00
Phenol	94	31.41	−9.46
n-Hexane	84	38.50	−1.28
Acetone	58	32.90	−15.64
n-propyl chloride	78.5	32.96	−15.49
nitrobenzene	123	37.71	−3.31
m-Toluidine	107	37.24	−4.51
Acetonitrile	41	25.93	−33.51
Water ($\Delta C/\Delta T = +2$)	18	8.49	−121.77

Downloaded At: 07:59 28 January 2011

TABLE V Values of $M^{1/2}(\Delta C/\Delta T)$ and percent degree of association for Alkanes, Alkenes, Alkynes, Alkyl phenyl ketone and Alkyl-*p*-xylyl-ketone

Substance		$\lvert M^{1/2}(\Delta C/\Delta T)\rvert$ $g^{1/2} ms^{-1} deg^{-1}$	$(\Delta L/L)$ 100%
A. Saturated Compounds	*n*-pentane	42.43	8.80
(Alkanes)	*n*-hexane	40.80	4.62
C_nH_{2n+2}	*n*-heptane	39.60	1.53
(n = 5 to 10, 12, 14, 16)	*n*-octane	41.80	7.18
	*n*-nonane	42.65	9.36
	n-decane	43.78	12.26
	n-dodecane	48.24	23.69
	tetra decane	50.65	29.67
	n-hexa decane	52.62	34.92
B. Olefins (Alkenes)	hexene	38.50	−1.28
C_nH_{2n}(n = 6 to 11, 13, 15)	heptene	41.58	6.62
	octene	44.45	13.97
	nonene	44.90	15.13
	decene	44.96	15.28
	undecene	49.64	27.28
	tridecene	52.61	34.90
	pentadecene	56.52	44.92
C. Acetylene derivatives	1-pentin	35.46	−9.08
(Alkyne)	1-hexin	42.56	9.13
C_nH_{2n-2}	1-heptin	43.11	10.54
(n = 5 to 8, 10, 12)	1-octin	45.10	15.64
	1-decin	45.81	17.46
	1-dodecin	48.96	25.54
D. Alkyl-Phenyl-Ketone	methylphenylketone	40.53	3.92
(Alkyne)	ethylphenylketone	42.83	9.82
$C_{n+p}H_{n+2p}O$	propylphenylketone	40.15	2.95
$\left(\begin{matrix} n = 8 \text{ to } 15 \\ p = 0 \text{ to } 7 \end{matrix}\right)$	butylphenylketone	45.82	17.49
	amylphenylketone	45.11	15.67
	hexaylphenylketone	44.11	13.10
	heptylphenylketone	42.85	9.87
	octylphenylketone	51.68	32.51
E. Alkyl-*p*-Xylyl-Ketone	methylketone	46.23	18.54
	ethylketone	45.82	17.49
	propylketone	49.09	25.87
	butylketone	53.76	37.85
	anylketone	54.27	39.15
	hexylketone	54.63	40.08
	heptylketone	54.83	40.59
	octylketone	55.12	41.33
	nonylketone	56.44	44.72

Downloaded At: 07:59 28 January 2011

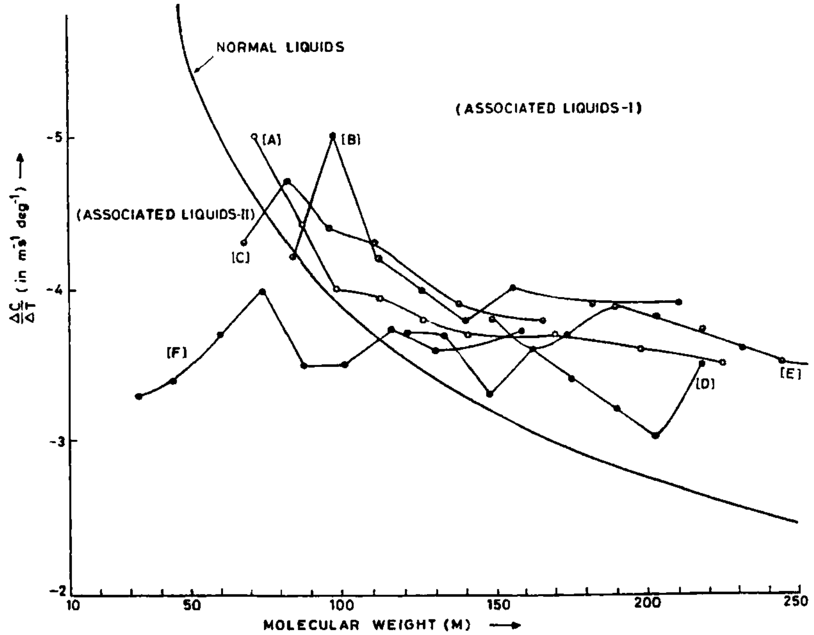


FIGURE 3 Temperature variation of ultrasonic velocity ($\Delta C/\Delta T$) *versus* molecular weight for (A) Alkane; (B) Alkene; (C) Alkyne; (D) Alkyl-phenyl-ketone; (E) Alkyl *p*-Ketone; (F) Alkohol: (Tab. V).

Downloaded At: 07:59 28 January 2011

for $\Delta M = 90$. The degree of association with positive sign ($|\Delta C/\Delta T| - 39$) may be characterized as those having associative characteristic – I. I dominated by attractive forces which may be London-dispersion type as a function of polarizability and ionization energy of molecules, their mutual potential energy depending upon their permanent dipole moment and induced dipole moments. The combined effect may be due to Van de Waal binding exhibiting association and departures from London-dispersion forces. Those liquids with negative sign of ($\Delta L/L$) 100% are classified as associated liquids II. Class – I category also include methanol, ethanol, *n*-propanol, *n*-butanol, *n*-pentanol and *n*-hexanol. There seems some other dominating forces for class – II like chemical bonding in addition to the forces mentioned for associated liquids I.

Water molecule has entirely different property because it has positive value of ($\Delta C/\Delta T$) *i.e.*, the temperature variation of ultrasonic velocity is +2. The value of $M^{1/2}(\Delta C/\Delta T)$ for water is +8.49 and therefore degree of association is −78.2 percent. The negative value of $(\Delta L/L)$ represents hydrogen bonding as found in water and the alcohols mentioned under class – II here above.

4. CONCLUSIONS

The present work is important and the qualitative description given on the basis of empirical theoretical treatment is fruitful in understanding the molecular interactions and the classification of organic liquids. Consideration of a suitable potential including the short range interactions of a tagged molecule through the state of broken or intact hydrogen bonds in pure liquids may enhance the rigor of the present work however, there may not be much quantitative change on the macroscopic scale.

Downloaded At: 07:59 28 January 2011

Acknowledgement

The author (MJ) is grateful to the University Grants Commission for financial assistance.

References

[1] Johri, M., Johri, G. K. and Roberts, J. A. (1991). *Phys. Chem. Liq.*, **24**, 71.

[2] Hirschfelder, J. O. (1967). Intermolecular Forces, John Wiley and Sons (New York).

[3] Anderson, D. J. E. (1967). *J. Chem. Phys.*, **47**, 4879.

[4] Bertolini, D., Cassettari, M., Ferrario, M., Grigolini, P. and Salvetti, G. (1985). *Adv. Chem. Phys.*, **62**, 277.

[5] Bertolini, D., Cassettari, M., Ferrario, M., Grigolini, P., Salvetti, G. and Tani, A. (1989). *J. Chem. Phys.*, **91**, 1179.

[6] Nosdrev, V. F., Application of Ultrasonics in Molecular Physics, Gordon and Breach (New York, 1963).

[7] Schaaffs, W., Molecular Acoustics, Springer Verlag (New York, 1967), Vol. 5.

[8] Lagemann, R. T., McMillan, D. R. and Woolf, W. E. (1949). *J. Chem. Phys., N.Y.*, **17**, 369.