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Isotopic effects on non-linearity, molecular radius and intermolecular free length

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Abstract. Computation of non-linearity parameter (B/A), molecular radius (r_{m}) and intermolecular free length (L_{f}) for H_2O, C_6H_6, C_6H_{12}, CH_3OH, C_2H_5OH and their deuterium-substituted compounds have been carried out at four different temperatures, viz., 293.15, 303.15, 313.15 and 323.15 K. The aim of the investigation is an attempt to study the isotopic effects on the non-linearity parameter and the physicochemical properties of the liquids, which in turn has been used to study their effect on the intermolecular interactions produced thereof.

Keywords. Non-linearity parameter; molecular radius; free length; intermolecular interactions.

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1. Introduction

The study of various physicochemical properties of isotopic substances is of significant importance due to their vast application in atomic technology, nuclear physics, chemistry, biology and other sciences. Out of the various stable isotopes, of special significance are the compounds of deuterium, which produced in the form of heavy water is used in nuclear reactors and is about to become an important fuel analog for possible control of thermonuclear processes. Various physicochemical properties, viz., molecular polarizability, molal volume, compressibility, heat capacity etc. have been carried out on more than twenty liquid substances [1] to study the effect of replacement of hydrogen by deuterium. In our previous investigation [2], computation of isothermal compressibility (β_{T}), coefficient of thermal expansion (α), Grüneisen parameter (Γ), internal pressure (P_{i}) and surface tension (σ) for H_2O, C_6H_6, C_6H_{12}, CH_3OH, C_2H_5OH and their deuterium-substituted compounds were

carried out at four different temperatures, viz., 293.15, 303.15, 313.15 and 323.15 K respectively. A recent revival in the interest regarding the study of non-linearity parameter (B/A) [3,4], molecular radius (r_{m}) [5] and intermolecular free length (L_{f}) [6–8] has prompted us to extend [2] our ongoing investigation for the aforementioned compounds.

2. Theoretical

Non-linearity parameter (B/A) has been calculated using the relation [4]

$$\frac{B}{A} = 2\gamma K'' + 2K, \tag{1}$$

where K and K'' represent the isobaric and isochoric acoustical parameters respectively and are given by

$$K'' = \left(1 + \frac{X}{2\beta T}\right) \quad \text{and} \quad K = \frac{1}{2}\left(1 + \frac{S^*(1+\alpha T)}{\alpha T}\right),$$

where $S^* = 1 + \frac{4}{3}\alpha T$.

Computation of molecular radius has been carried out by employing the relation

$$r = A\left[1 - \beta\left\{\left(1 + \frac{1}{3\beta}\right)^{1/2} - 1\right\}^{1/3}\right], \tag{2}$$

where $A = (3V/16\pi N)^{1/3}$ and $\beta = \gamma RT/Mu^2$ where all the symbols have their usual meaning.

Intermolecular free length (L_{f}) has been computed by using the equation [7]

$$L_{\mathrm{f}} = \frac{2V_{\mathrm{a}}}{Y} \tag{3}$$

where V_{a} is the available volume and Y is the surface area per mole given by

$$Y = (36\pi N V_{\mathrm{a}}^2)^{1/3}, \tag{4}$$

where N is the Avogadro's number, and

$$V_{\mathrm{a}} = \frac{V}{K' + 1}$$

$$K' = \frac{1}{2}\left(\frac{3 + S^*(1+\alpha T) + X)}{\alpha T}\right)$$

and

$$X = -\frac{2(1+2\alpha T)}{\tilde{V}^{C_1}},$$

where

$$\tilde{V} = \left[1 + \frac{\alpha T}{3(1+\alpha T)}\right]^3 \quad \text{and} \quad C_1 = \frac{13}{3} + \frac{1}{\alpha T} + \frac{4\alpha T}{3}.$$

3. Results and discussion

In the present investigation, computation of three parameters, viz., non-linearity parameter (B/A), molecular radius (r_m) and intermolecular free length (L_f) for H_2O, C_6H_6, C_6H_{12}, CH_3OH, C_2H_5OH and their corresponding deuterium-substituted compounds have been made at four different temperatures, viz., 293.15, 303.15, 313.15 and 323.15 K. The values of ultrasonic velocity, density and adiabatic compressibility of the hydrogen compounds and their corresponding deuterium compounds have been taken from [3]. All the aforementioned parameters which have been computed are represented in table 1.

A look at the B/A values for all the liquids under consideration shows that the non-linearity parameter values register decrease with an increase in the temperature and the values seem to be on the higher side for the deuterium compounds as compared to the hydrogen analogs. A closer look at the values further reveals that the difference in values are not pronounced in the case of CH_3OH and CH_3OD and in the case of C_2H_5OH and C_2H_5OD. The reason attributed to this behaviour may be due to the values of ultrasonic velocity and adiabatic compressibility which clearly indicates that for all the deuterocompounds under consideration, the sound propagation is slower as compared to their hydrogen analogs. Meanwhile, the compressibility values are higher than that of hydrogen compounds. Another factor responsible for the B/A values may be the previously predicted [2] pseudoGrüneisen parameter values which are seem to be on the higher side for all deuterium compounds. The higher values for the deuterium compounds indicate an increase in the anharmonicity arising in the lattice.

Molecular radii (r_m) also show higher values for the deuterium compounds as compared to the hydrogen analogs and the values seem to be more or less constant with temperature variation. The same trend can be seen in the intermolecular free length (L_f) values. However, the values here register an increasing trend with increase in temperature which is very reasonable. Both the r_m and L_f values are found to be maximum for C_6H_{12} and its deuterium-substituted analog, C_6D_{12}.

At low temperatures, the difference in the molal volume of isotopic substances is determined by the difference in the zero-point energy of oscillations of their molecules. At elevated temperatures, it is determined by the difference in the van der Waals forces. This results in the fact that in the region of standard thermodynamic temperature, the replacement of hydrogen by deuterium either hardly changes the molal volume or produces a certain increase. Among the deuterium compounds under investigation, benzene, toluene and cyclohexane differ somewhat in this respect. Further at low temperature, for liquids with low molecular weights, the decease in the intermolecular distance as a result of the replacement of a light isotope by a heavy isotope affects the energy of the dispersion interaction more strongly than the decrease in electronic polarizability.

The decrease in molal volume when all six hydrogen atoms in benzene or even all twelve hydrogen atoms in cyclohexane molecule are replaced by deuterium at about 300 K is only 0.2 to 0.3%. For substances which are associated through hydrogen bonds there are additional reasons for the change in the intermolecular distance when the hydrogen atoms forming these bonds are replaced by deuterium. It has been shown [9,10] that this substitution produces an appreciable change in

length of hydrogen bond, i.e. O---O distance. This phenomenon is explained by two opposing effects.

(a) Due to anharmonicity in the values of oscillations of the O–H bond, the decrease in its zero-point energy when hydrogen is replaced by deuterium

Table 1. Values of non-linearity parameter (B/A), molecular radius (r_{m}) and intermolecular free length (L_{f}) of pure liquids and its isotopes at different temperatures.

T (K)	u (m/s)	α (10^{-3} K^{-1})	B/A	r_{m} (mol radii) (10^{-8} m)	L_{f} (Å)
H_2O					
293.15	1483	1.045	7.38	1.17	0.750
303.15	1511	1.031	7.38	1.17	0.751
313.15	1531	1.021	7.37	1.17	0.752
323.15	1545	1.014	7.37	1.17	0.754
D_2O					
293.15	1386	1.062	7.40	1.19	0.766
303.15	1413	1.048	7.39	1.19	0.767
313.15	1434	1.038	7.39	1.19	0.768
323.15	1448	1.030	7.39	1.19	0.769
C_6H_6					
293.15	1327	1.128	7.37	1.97	1.223
303.15	1280	1.147	7.36	1.98	1.231
313.15	1232	1.167	7.35	1.98	1.238
323.15	1184	1.189	7.34	1.98	1.246
C_6D_6					
293.15	1246	1.150	7.39	2.00	1.242
303.15	1201	1.170	7.38	2.00	1.250
313.15	1156	1.191	7.38	2.00	1.257
323.15	1111	1.212	7.37	2.01	1.264
C_6H_{12}					
293.15	1280	1.172	7.35	2.07	1.281
303.15	1230	1.193	7.34	2.07	1.289
313.15	1180	1.217	7.32	2.07	1.297
323.15	1130	1.242	7.31	2.07	1.304
C_6D_{12}					
293.15	1153	1.208	7.38	2.11	1.315
303.15	1110	1.229	7.38	2.11	1.323
313.15	1068	1.251	7.37	2.12	1.330
323.15	1026	1.274	7.35	2.12	1.338
CH_3OH					
293.15	1122	1.248	7.36	1.48	0.952
303.15	1089	1.265	7.35	1.48	0.957
313.15	1057	1.282	7.33	1.48	0.962
323.15	1024	1.301	7.32	1.48	0.967
CH_3OD					
293.15	1103	1.255	7.36	1.49	0.959
303.15	1071	1.271	7.35	1.49	0.964
313.15	1040	1.288	7.34	1.49	0.969
323.15	1008	1.306	7.32	1.49	0.974

contd...

Table 1. Contd...

T (K)	u (m/s)	α (10^{-3} K^{-1})	B/A	r_m (mol radii) (10^{-8} m)	L_f (Å)
C_2H_5OH					
293.15	1167	1.224	7.35	1.67	1.064
303.15	1133	1.241	7.34	1.68	1.070
313.15	1098	1.258	7.33	1.68	1.075
323.15	1064	1.276	7.31	1.68	1.081
C_2H_5OD					
293.15	1145	1.232	7.36	1.68	1.069
303.15	1111	1.248	7.35	1.68	1.074
313.15	1077	1.266	7.34	1.68	1.080
323.15	1043	1.284	7.32	1.69	1.085

produces a decrease in the corresponding valence distances. As a result of this, there is a decrease in the van der Waals radius of hydroxyl group and this weakens the repulsion forces between oxygen atoms in the system O–D–O relative to the system O–H–O thereby producing a decrease in O---O distance.

(b) Due to anharmonicity of oscillations of hydrogen atom in the system, O–H–O, the maximum probability curve of distribution for it is shifted to the right from the minimum on the potential energy curve. Since the curve does not change when hydrogen is replaced by deuterium, and the zero-point energy of oscillation falls, the shift of probability curve of the distribution for the deuterium atoms is less than that for hydrogen atom. This results in the weakening of attractive forces between the D---O atoms relative to the same forces between H---O atoms and thus on replacement of hydrogen by deuterium, there is some increase in O---O distance.

The third factor responsible for a change in the intermolecular distance on replacement of hydrogen forming the hydrogen bond by deuterium in cases where the density of the steric arrangement of the atoms is low, may increase with disordering. This phenomenon is particularly probable for molecular liquids in which the formation of a lattice or another form of order is apparently associated with an increase in the deviation from the closest packing of the molecules and hence with some expansion.

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