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THERMOACOUSTIC AND THERMODYNAMIC PROPERTIES OF HIGHER N-ALKONALS

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A theoretical model is developed and used to calculate the values of thermoacoustic and thermodynamic parameters of higher n-alkanols. This model needed only the knowledge of volume expansivity of these liquids.

KEYWORDS : Acoustical parameters, volume expansivity, available volume, molecular constant.

INTRODUCTION

The study of thermoacoustic and thermodynamic properties of higher *n*-alkanols are of current interest due to their potential and wide range of application involving hydrocarbon or petroleum fluids [1]. These are used as coserfactants in oil in-water emulsion [2], as additives in gasoline to reduce pollution effect [3], as in-hibitars to prevent the precipitation of gas hydrates in pipe lines [4], and as co-solvent in supper critical fluid technology [5-8]. Thermoacoustic and thermodynamic properties are useful in studying the internal structure, molecular order and non-linear behaviour of organic liquids [9-14]. They also provide a deeper understanding about the intermolecular forces operative in liquids [15-17]. The studies [16, 18] suggest that molecules of a liquid are not rigid spheres that transmit acoustic energy instantaneously from one molecular bond to the next without a time delay consequently, the potential forces *i.e*. intramolecular forces within molecules are of as much importance in sound propagation as are intermolecular forces between the molecules. Thus there are two distinct modes of vibration namely, (i) intermolecular acoustic modes, and (ii) the intramolecular optic modes.

Thermoacoustic and thermodynamic properties are directly related with the molecular force constant governing the intermolecular and intramolecular energy, and can be expressed in terms of volume expansion which has been found as the controlling factor for their dependence on temperature and volume of liquids [19]. Using this concept, we have developed and used a theoretical model to investigate thermoacoustic and thermodynamic properties of higher *n*-alkanols, for which no experimental data is required, except the volume expansivity.

THEORY

Assuming that sound velocity is a function of both volume and temperature the isobaric (K), isothermal (K') and isochoric (K'') acoustical parameters can be related as

$$K' = K + K'' \quad \ldots (1)$$

These parameters can also be expressed in terms of volume expansivity as follows [20] :

$$K = \frac{1}{2}\left[1 + \frac{S^*(1+\alpha T)}{\alpha T}\right] \quad \ldots (2)$$

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

and $$K'' = 1 + \left[\frac{X}{2\alpha T}\right] \quad \ldots (4)$$

where $$S^* = 1 + \frac{4\alpha T}{3} \quad \ldots (5)$$

$$X = \frac{-2(1+2\alpha T)}{\tilde{V}^{Cl}} \quad \ldots (6)$$

$$\tilde{V} = \left[1 + \frac{\alpha T}{3(1+\alpha T)}\right]^3 = \left(\frac{S^*}{1+\alpha T}\right)^3 \quad \ldots (7)$$

and $$C_1 = \frac{13}{3} + \frac{1}{\alpha T} + \frac{4\alpha T}{3} \quad \ldots (8)$$

In the above expressions X is the isochoric temperature coefficient of internal pressure in the zero pressure limit, $(\tilde{V})^{\mathrm{Cl}} = \tilde{\beta}$ is the reduced compressibility, $\tilde{V} = \frac{V}{V^*}$ is the reduced volume and C_1 is the pressure derivative of isothermal bulk modulus, which is known as Moelwyn Hughes parameter.

The available volume (V_a) can be expressed in terms of acoustical parameters as [12, 21].

$$\frac{V_a}{V} = (K'+1)^{-1} = (K''+K+1)^{-1} \quad \ldots (9)$$

The repulsive exponent of inter molecular potential can be expressed as [22]

$$n = 3\left[\frac{2}{V_f} - 5\right] \quad \ldots (10)$$

where $V_f = \frac{V_a}{V}$ is the fractional free volume

Equation (9) can be written in terms of acoustical parameters as

$$n = 3[2(K'+1) - 5] \quad \ldots (11)$$

The molecular constant (n') is defined as [16]

$$\frac{1}{n'} = \frac{1}{2}\left(\frac{d\ln P_i}{d\ln T}\right)_v + 1 \quad \ldots (12)$$

where $$\left(\frac{d\ln P_i}{d\ln T}\right)_v = 2(K''-1)\alpha T \quad \ldots (13)$$

is the isochoric temperature coefficient of internal pressure, equations (12) and (13), yield

$$n' = [(K'' - 1)\,\alpha T + 1]^{-1} \quad \ldots (14)$$

Result and discussions

The experimental values of volume expansivity of four higher *n*-alkanols viz. Heptanol, Octanol, Nonanol and Decanol are taken from the literature (23). These values are listed in table 1, at atmosphere peressure and temperature T = 293.15 K. Using these values of in equations (1-8), we have calculated the values of reduced volume ($\tilde{V}$), Moelwyn-Hughes parameter C_1, reduced compressibility ($\tilde{\beta}$), isochoric temperature coefficient of internal pressure (X), isobaric (K), isothermal (K') and isochoric (K'') acoustical parameters. These values are reported in table 1 for all the four liquids. It is observed from the table that the values of α, $\tilde{V}$ and $\tilde{\beta}$ decreases significantly in going from heptanol to decanol. On the other hand the values of C_1 increases accordingly. It might be due to increase in chain-length by a $-CH_2$ intervening group, in going from heptanol to decanol in the homologous series of alkanols. The large values of C_1 are indicative of dissociative nature of these liquids [24]. The values of $\tilde{\beta}$ are found in the range 5 to 6, as reported in the literature [21]. The value of X is also found in the range, as reported in the literature [11] for organic liquids. The values of acoustical parameters K and K' are found comparable with eachother, and K is larger than K'. On the other hand K'' is found negative for all these liquids. It is indicative to the negative contribution of K'' to thermocoustic properties. The values of the ratio $\left(\frac{K}{K'}\right)$ are found about unity for all the liquids, as suggested by Nomoto [25].

Table 1. Thermoacoustic Parameters of Higher *n*-alkanols at P = 0.1 MPa and T = 293.15 K

Liquid	[23] $\frac{\alpha}{10^{-3}\,K^{-1}}$	$\tilde{V}$	C_1	$\tilde{\beta}$	X	K	K'	K''	$K'K$
Heptanol	0.8477	1.2125	8.6850	5.3310	– 0.5616	3.8436	3.7136	– 0.1300	1.0350
Octanol	0.8291	1.2084	8.7676	5.2576	– 0.5654	3.8854	3.7225	– 0.1629	1.0438
Nonanol	0.8241	1.2074	8.7912	5.2429	– 0.5658	3.8972	3.7262	– 0.1709	1.0459
Decanol	0.8116	1.2048	8.8507	5.2018	– 0.5674	3.9270	3.7345	– 0.1926	1.0516

Using the calculated values of acoustical parameters K, K' and K'' in equations (9), (11) and (14), we have calculated the values of the fractional free volume $V_f = \left(\frac{V_a}{V}\right)$, repulsive exponent of intermolecular potential (n) and molecular constant (n'). These values are reported in table 2 for all four liquids. The values of V_f are found to remain constant about 0.212 for all the liquids. The fractional free volume V_f is a measure of disorder due to increased mobility of molecules [22]. The comparison with the literature [9-12, 26] reveals that these

liquids are highly disordered liquids due to high values of V_f. The values of n are found to vary from about 13.26 to 13.41, which are consistent with the range from 13 to 19, as reported in the literature [26] for hydrocarbon liquids. comparison with other liquids [27] reveals that higher alkanols have low values of *n*, which is indicative of the presence of strong repulsive forces in these liquids [28]. The parameter *n* has also been used as a measure of anharmonicity in the organic liquids [22]. In the present study the values of *n* increases significantly from heptanol to decanol. It shows that anharmonicity increases in going from heptanol to decanol in the homologous series of alkanols. The values of molecular constant (*n*') remains constant around 1.39 for all the liquids.

Table 2. Thermodynamic Parameters of Higher n-alkanols at P = 0.1 MPa and T = 293.15 K

Liquid	$\frac{V_a}{V}$	*n*	*n*'
Heptanol	0.2122	13.2752	1.3904
Octanol	0.2118	13.3286	1.3941
Nonanol	0.2116	13.3554	1.3945
Decanol	0.2112	13.4091	1.3961

Conclusion

The proposed model to calculate the thermoacoustic and thermodynamic parameter is simple as it needed only the experimental values of volume expansivity, and gives consistent results of these parameters. From this study it is observed that these higher alkanols are of dissociative nature and highly disordered liquids.

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