Estimation of Sharma Constant and Thermoacoustic Properties of Fatty Acids

M.S.R. Subrahmanyam[a], **H. Sumathi Vedanayagam**[b], **D. Venkateshwar Rao**[b],
A. Rajaiah[b], **and P. Venkatacharyulu**[c,*]
[a]Pragathi Mahavidyalaya College, [b]Indian Institute of Chemical Technology, Hyderabad, and [c]Department of Physics,
Nagarjuna University, Nagarjunanagar, Guntur - 522 510, India

ABSTRACT: From the volume expansivity α, a number of thermoacoustic parameters, including the Sharma constant, S_0, are estimated for four fatty acids as a function of temperature. The Sharma constant, which was established to be a constant with the characteristic value 1.11 ± 0.01 over a number of systems investigated by earlier investigators, is also found to be a constant with the same value for all fatty acids under investigation. Further, the Sharma constant, S_0, is independent of temperature and dependent only on α. All other parameters estimated are discussed and compared with the values reported in the literature by earlier workers for different systems.
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KEY WORDS: Density, fatty acids, Huggin's Parameter, isochoric temperature coefficient of internal pressure, isochoric temperature coefficient of volume expansion, reduced compressibility, reduced volume, Sharma constant, thermoacoustic properties, volume, volume expansivity.

The importance of the thermoacoustic parameters and their estimation from the volume expansivity α has been studied by earlier investigators over a number of systems. In continuation of the work on thermoacoustic parameters by using the volume expansivity for certain vegetable oils, we report here thermoacoustic parameters estimated from only the volume expansivity α for myristic acid, oleic acid, palmitic acid, and stearic acid.

These parameters will help elucidate some thermodynamic and rheological properties that are necessary for the fatty acid industry. This study was undertaken because fatty acids are constituents of oils; further, physical properties, such as density and viscosity of the fatty acids, are important in their evaluation as alternatives for diesel fuels.

The densities at various temperatures for these fatty acids are reported by Islam and Ahmed (1). From the density/temperature data, the authors estimated the volume expansivity at various temperatures for all fatty acids under investigation.

THEORY

The Sharma constant, S_0, relates the isothermal volume derivative of intermolecular constant to the thermodynamic Gruneisen parameter. It is an important parameter for investigating the physicochemical behavior of any system which, in turn, will help in understanding the molecular order and intermolecular interactions in the condensed phase. Reports by Sharma (2–5), Sharma and Reddy (6,7), and Venkatacharyulu *et al.* (8–10) show that the value of S_0 is constant for any system, either in the liquid or in the solid state. From their investigations, Venkatacharyulu *et al.* (8–10) concluded that even in the mesomorphic state, where the mesogens simultaneously exhibit the rheological properties of liquids as well as the anisotropic properties of crystals, S_0 is again a constant, with the same characteristic value as was reported by Sharma (2–5) and Sharma and Reddy (6,7) for certain nonmesomorphic systems.

Venkatacharyulu *et al.* (8–10) observed from their studies that S_0 assumes a lower than characteristic value only at and in the immediate vicinity of the transition temperature, when the system changes from an isotropic liquid state to a mesomorphic state (nematic or smectic), i.e., from a completely disordered low-density isotropic liquid state to a more ordered (orientationally or positionally, as the case may be) dense state. S_0 drops more exactly at the transition temperature than at any other temperature.

Because the Sharma constant and other related parameters have not been estimated for the fatty acids as of yet, in the present studies the authors estimated certain thermodynamic parameters, such as the isochoric temperature coefficient of volume expansion, the isochoric temperature coefficient of internal pressure, the reduced volume, the reduced compressibility, and the Huggin's parameters. These parameters may help in characterizing the fatty acids, when the densities are taken from the literature (2–10).

Very recently, Murthy (11) estimated all the thermoacoustic parameters mentioned earlier, including S_0, for a number of molecular liquids, associated liquids, and aqueous solutions, and observed that S_0 is also constant for all molecular liquids and associated liquids, and the behavior of all param-

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*To whom correspondence should be addressed.

eters in aqueous solutions is slightly different when compared to the molecular liquids.

Isochoric temperature coefficient of internal pressure $[\mathrm{d}\ln P_i/\mathrm{d}\ln T]_V$. To discuss the estimation of the isochoric temperature coefficient of internal pressure, it is necessary to mention the estimation of volume expansivity. The volume expansivity α can be written as:

$$\alpha = \frac{1}{V_n}\frac{\Delta V}{\Delta T} \qquad [1]$$

where $\Delta V = (V_2 - V_1)$, $\Delta T = (T_2 - T_1)$, and $V_n = (V_1 + V_2)/2$. V_2 and V_1 are the molar volumes at temperature T_2 and T_1, respectively. In previous work (12), α was calculated from volume and density measurements as functions of temperature at intervals of 10 K.

Haward and Parker (13) obtained an expression for the isochoric temperature coefficient of internal pressure, and later Sharma (14) obtained an expression for the isochoric temperature coefficient of internal pressure in terms of α:

$$\left[\frac{\mathrm{d}\ln P_i}{\mathrm{d}\ln T}\right]_V = \frac{2}{\beta}\left[\frac{\mathrm{d}\ln\alpha}{\mathrm{d}\ln T}\right]_V = \frac{-2(1+2\alpha T)}{(\tilde{V})^{C_1}} \qquad [2]$$

where P_i is the internal pressure and $\tilde{\beta} = \beta/\beta^*$ is the reduced compressibility. β is the compressibility at absolute temperature T, and β^* is the characteristic compressibility at absolute zero temperature and zero pressure. $\tilde{V}$, C_1 and α are the reduced volume, pressure coefficient of bulk modulus, and volume expansivity at temperature T and pressure P, respectively. $\tilde{V}$ and C_1 are as defined below. The authors adopted this equation and estimated the parameter $[\mathrm{d}\ln P_i/\mathrm{d}\ln T]_V$.

Isochoric temperature coefficient of volume expansion $[\mathrm{d}\ln \alpha/\mathrm{d}\ln T]_V$. The isochoric temperature coefficient of volume expansion can be expressed as:

$$\left[\frac{\mathrm{d}\ln\alpha}{\mathrm{d}\ln T}\right]_V = -S^* S_0^* = -(1+2\alpha T) \qquad [3]$$

where S^* and S_0^* are the Sharma parameters, as defined later.

The pressure coefficient of bulk modulus, C_1, which is dimensionless, was introduced by Moelwyn-Hughes (15) as:

$$C_1 = \left[\frac{\mathrm{d}}{\mathrm{d}p}\left(\frac{1}{\beta}\right)\right] = \left[\frac{\mathrm{d}\ln\beta}{\mathrm{d}\ln V}\right]_T \qquad [4]$$

Sharma (16) obtained the compressibility expression from the reduced equation of state to estimate C_1. The values of $\tilde{\beta}$ and α were calculated according to the expressions:

$$\tilde{\beta} = \frac{\alpha T \tilde{V}^2}{P^*} \qquad [5]$$

$$\alpha = 3\left(\frac{\tilde{V}^{1/3} - 1}{T\left(4 - 3\tilde{V}\right)^{1/3}}\right) \qquad [6]$$

where $\tilde{V} = V/V^*$ is the reduced volume, V is the molar volume, V^* is the characteristic volume, and P^* is the characteristic pressure. In the present work, α was calculated from Equation 1 by using the temperature and density data reported by Islam and Ahmed (1).

Reduced volume, $\tilde{V}$. The reduced volume, $\tilde{V}$, a function of the volume expansivity α and temperature in Equation 6, is:

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

Sharma used Equations 4, 5, and 6 and estimated C_1 in terms of only α and T.

$$C_1 = \left[\frac{13}{3} + (\alpha T)^{-1} + \frac{4}{3}\alpha T\right] \qquad [8]$$

It can be concluded that α is the controlling factor of C_1 and, as such, is an important parameter to estimate the temperature dependence of C_1.

Reduced compressibility $\tilde{\beta}$. The isochoric temperature coefficient of compressibility $\tilde{\beta}$ can be obtained from Equations 2 and 3 as:

$$\left[\frac{\mathrm{d}\ln\beta}{\mathrm{d}\ln T}\right]_V = \frac{2\left[1 - 2\alpha T\left(\tilde{V}^{C_1} - 1\right)\right]}{(\tilde{V})^{C_1}} + 2\alpha T \qquad [9]$$

and from Sharma and Reddy (7) the reduced compressibility is:

$$\tilde{\beta} = \tilde{V}^{C_1} \qquad [10]$$

The Sharma constant, S_0. Sharma expressed S_0 as:

$$S_0 = -\frac{1}{2}\left(\frac{\mathrm{d}\ln P_i}{\mathrm{d}\ln T}\right)_V\left(\frac{\tilde{\alpha}}{\tilde{V}}\right) = \frac{S^* S_0^* \;\tilde{\alpha}}{\tilde{\beta}\tilde{V}} = \frac{(1+2\alpha T)}{\tilde{V}^{C_1}}(3+4\alpha T) \qquad [11]$$

When the parameters $\tilde{\alpha}$, S^*, and S_0^* are expressed in terms of α only, Sharma obtained:

$$S^* = \frac{\tilde{\alpha}}{3\tilde{V}} = 1 + \frac{4}{3}\tilde{\alpha}\tilde{T} = 1 + \frac{4}{3}\alpha T \qquad [12]$$

$$S_0^* = \frac{-\left(\frac{\mathrm{d}\ln\alpha}{\mathrm{d}\ln T}\right)_V}{S^*} = \frac{1+2\alpha T}{1+\frac{4}{3}\alpha T} \qquad [13]$$

$$\tilde{\alpha} = \left(\frac{\mathrm{d}\ln\tilde{V}}{\mathrm{d}\tilde{T}}\right) = \alpha T^* \qquad [14]$$

$$\tilde{T} = \frac{T}{T^*} = \frac{\tilde{V}^{\frac{1}{3}} - 1}{\tilde{V}^{\frac{4}{3}}} \qquad [15]$$

$$\frac{\tilde{V}^{\frac{1}{3}}}{(\tilde{V}^{\frac{1}{3}}-1)}=(\tilde{V}\tilde{T})^{-1}=\frac{(3+4\alpha T)}{\alpha T}=\frac{3S^*}{\tilde{\alpha}\tilde{T}}=\frac{3S^*}{\alpha T} \qquad [16]$$

where $\tilde{\alpha}$ represents the reduced volume expansivity, $\tilde{T}$ is the reduced temperature, and T^* is the characteristic temperature of the substance.

Sharma (2–5), Sharma and Reddy (6,7), Venkatacharyulu *et al.* (8–10), and Murthy (11) have shown that S_0 is a constant, independent of temperature and dependent only on the coefficient of volume expansion α.

Huggins parameter F. Huggins (17,18) obtained a parameter which may be expressed in terms of temperature and pressure derivatives of compressibility as:

$$F=1+\frac{2}{3}\alpha T+T\left(\frac{\mathrm{d}\ln\beta}{\mathrm{d}T}\right)_P+\left(\frac{\alpha T}{\beta}\right)\left(\frac{\mathrm{d}\ln\beta}{\mathrm{d}P}\right)_T \qquad [17]$$

If the compressibility is assumed to be a function of only volume and temperature, according to Sharma (5), it can be shown from the thermodynamic considerations that:

$$\frac{\alpha}{\beta}\left(\frac{\mathrm{d}\ln\beta}{\mathrm{d}P}\right)_T+\left(\frac{\mathrm{d}\ln\beta}{\mathrm{d}T}\right)_P=\left(\frac{\mathrm{d}\ln\beta}{\mathrm{d}\ln T}\right)_V \qquad [18]$$

From Equations 9, 10, 17, and 18 it follows that:

$$F=1+\frac{2}{3}\alpha T+T\left(\frac{\mathrm{d}\ln\beta}{\mathrm{d}T}\right)_V=1+\frac{2}{\tilde{V}^{C_1}}+(4\alpha T)\left[\frac{2}{3}-\frac{(\tilde{V}^{C_1}-1)}{\tilde{V}^{C_1}}\right] \qquad [19]$$

From Equations 11 to 13 and 19, the Huggins parameter, F, can also be expressed in terms of S_0 as well as the Sharma parameters S^* and S_0^*. All parameters can again be expressed in terms of the single measurable parameter α:

$$\begin{aligned}F&=2\left[1+\frac{S_0}{3S^*}\right]-S^*=2\left(1+\frac{\alpha T}{3}\right)-S_0^*S^*+\frac{2S_0}{3S^*}\\&=1-\frac{2\alpha T}{3}-S^*(S_0^*-1)+\frac{2S_0}{3S^*}\end{aligned} \qquad [20]$$

From Equations 11 and 13, S_0 can also be expressed as:

$$S_0=-\left(\frac{\mathrm{d}\ln\alpha}{\mathrm{d}\ln T}\right)_V\frac{\tilde{V}_0}{\tilde{V}^2}=\frac{S^*S_0^*\tilde{V}_0}{\tilde{V}^2} \qquad [21]$$

where $\tilde{V}_0=\tilde{\alpha}\tilde{V}/\tilde{\beta}$.

It is evident from these equations that α, the volume expansivity, is an important parameter that can be used to estimate the various physical parameters, S_0, S^*, S_0^*, and F.

TABLE 1
Thermal Properties and Sharma Constant (S_0) and Parameters for Four Fatty Acids[a]

Temperature K	$\alpha \times 10^3$	$\left(\frac{\mathrm{d}\ln P_i}{\mathrm{d}\ln T}\right)_V$	$\left(\frac{\mathrm{d}\ln\alpha}{\mathrm{d}\ln T}\right)_V$	$\tilde{V}$	$\tilde{\beta}$	S_0	S^*	F
Oleic acid								
298.15	0.7849	−0.569	−1.467	1.201	5.153	1.12	1.311	1.257
303.15	0.8025	−0.564	−1.486	1.208	5.268	1.12	1.324	1.239
313.15	0.809	−0.558	−1.506	1.215	5.395	1.12	1.337	1.220
323.15	0.8156	−0.552	−1.526	1.223	5.526	1.12	1.351	1.201
353.15	0.8359	−0.535	−1.59	1.245	5.943	1.118	1.393	1.141
363.15	0.8403	−0.529	−1.612	1.253	6.08	1.117	1.408	1.121
373.15	0.8501	−0.523	−1.634	1.26	6.245	1.116	1.422	1.100
383.15	0.8453	−0.519	−1.647	1.265	6.34	1.116	1.431	1.088
393.15	0.877	−0.509	−1.689	1.278	6.636	1.114	1.459	1.049
403.15	0.86	−0.508	−1.693	1.28	6.663	1.114	1.462	1.046
413.15	0.88	−0.499	−1.726	1.29	6.91	1.112	1.484	1.015
Stearic acid								
348.15	0.8515	−0.534	−1.592	1.246	5.96	1.118	1.395	1.139
353.15	0.8829	−0.526	−1.623	1.256	6.171	1.117	1.415	1.110
363.15	0.8786	−0.522	−1.637	1.261	6.27	1.116	1.425	1.097
373.15	0.8864	−0.516	−1.661	1.269	6.434	1.115	1.44	1.075
383.15	0.8943	−0.51	−1.685	1.277	6.604	1.114	1.456	1.053
393.15	0.9024	−0.504	−1.709	1.285	6.78	1.113	1.472	1.031
403.15	0.9106	−0.498	−1.734	1.293	6.963	1.112	1.489	1.008
413.15	0.919	−0.491	−1.759	1.301	7.152	1.111	1.506	0.985
423.15	0.9275	−0.485	−1.784	1.309	7.35	1.109	1.523	0.962
Palmitic acid								
338.15	0.8449	−0.54	−1.571	1.239	5.816	1.118	1.38	1.159
353.15	0.8594	−0.53	−1.606	1.251	6.056	1.117	1.404	1.126
363.15	0.8669	−0.524	−1.629	1.258	6.211	1.117	1.419	1.105
373.15	0.8745	−0.518	−1.652	1.266	6.372	1.116	1.434	1.083
383.15	0.8224	−0.524	−1.63	1.259	6.217	1.115	1.42	1.104
393.15	0.89	−0.506	−1.699	1.282	6.712	1.114	1.466	1.040
403.15	0.8855	−0.503	−1.713	1.286	6.813	1.113	1.475	1.027
413.15	0.9188	−0.491	−1.758	1.301	7.15	1.111	1.505	0.985
423.15	0.9017	−0.491	−1.762	1.302	7.18	1.111	1.508	0.9820
Myristic acid								
353.15	0.8567	−0.531	−1.604	1.25	6.045	1.117	1.403	1.127
363.15	0.8641	−0.525	−1.627	1.258	6.197	1.117	1.418	1.106
373.15	0.8594	−0.521	−1.641	1.262	6.295	1.116	1.427	1.094
383.15	0.8792	−0.513	−1.673	1.273	6.521	1.115	1.448	1.064
393.15	0.8745	−0.509	−1.687	1.278	6.621	1.114	1.458	1.051
403.15	0.8948	−0.501	−1.721	1.289	6.868	1.113	1.48	1.020
413.15	0.8902	−0.497	−1.735	1.293	6.973	1.112	1.49	1.007
423.15	0.911	−0.489	−1.77	1.304	7.24	1.11	1.513	0.9750

[a] See equations for further information on parameters.

RESULTS AND DISCUSSION

Isochoric temperature coefficient of internal pressure $[\mathrm{d}\ln P_i/\mathrm{d}\ln T]_V$. Table 1 shows that the isochoric temperature coefficient of internal pressure is a negative quantity for all fatty acids under study and increases slightly with a rise in temperature, but maintains a value of around 0.5. This is in accordance with the reports of earlier investigators for different systems. The isochoric temperature coefficient of internal pressure is a useful parameter for investigating condensed matter because this parameter will help in the estimation of n, the intermolecular constant. Constant n, which is the ratio of the internal pressure to the cohesive energy density, gives some information regarding intermolecular interactions in liquids. The total pressure of any system is the sum of the thermal pressure and internal pressure. Because the thermal pressure will be much less than the internal pressure, it can be neglected. Further, $[\mathrm{d}\ln P_i/\mathrm{d}\ln T]_V$ is small and difficult to estimate, but it can be measured and will give some information regarding either molecular order or disorder in liquids as a function of temperature.

Isochoric temperature coefficient of volume expansion [d ln α/d ln $T]_V$. The isochoric temperature coefficient of volume expansion is also negative, with a value ranging from −1.46 to −1.78. However, this parameter is also temperature-dependent and decreases with an increase in temperature for all fatty acids under consideration without any abnormalities with the variation of temperature. However, for myristic acid, the values of this parameter are less at all temperatures investigated compared to the other fatty acids (Table 1). Next, in order, are palmitic, stearic, and lastly, oleic acid. The reason for these variations from one fatty acid to the other can be attributed to differences in chainlength of the fatty acids.

Reduced volume $\tilde{V}$. Table 1 shows that this parameter varies between 1.20–1.31 for all fatty acids under study. However, this parameter is slightly higher for stearic acid. Next, in decreasing order, are myristic, palmitic, and oleic acid. This parameter is also temperature-dependent, increasing with increase in temperature.

Reduced compressibility $\tilde{\beta}$. Table 1 shows that the estimated values of $\tilde{\beta}$ are temperature-dependent, increasing with increasing temperature, and the value of this parameter varies between 5.2–7.3. This parameter ranges from 3.1 to 5.6 for various oils investigated by the authors.

Sharma constant S_0. Table 1 shows that S_0 is independent of temperature for all fatty acids investigated and has the same characteristic value of 1.11 ± 0.01. The value of S_0 is within the established range. Further, the authors noticed that any slight variation in α did not affect the value of S_0. This enables the authors to conclude that S_0 is also a constant for all fatty acids under investigation, with the same characteristic constant value as was reported for the other systems investigated by earlier workers.

Values of the Sharma parameter S^* calculated for the fatty acids under study range from 1.31 to 1.52. This parameter is also temperature-dependent and increases with increase of temperature. The value of S^* for stearic acid at all temperatures investigated is slightly higher when compared to the values observed in the other fatty acids.

Huggins parameter F. The Huggins parameter F as estimated from either Equation 19 or 20 for all fatty acids under investigation can be found in Table 1. F is slightly temperature-dependent and decreases with an increase in temperature. Further, the values of F investigated at any temperature for stearic acid are less when compared to the other fatty acids.

The authors successfully adopted this method and obtained the various thermoacoustic parameters from only the volume expansivity for the four fatty acids reported here.

Table 1 shows that the Sharma constant, S_0, is independent of temperature and dependent on α. These studies reveal that even for fatty acids, which are long-chain molecules and are associated in general through hydrogen bonding, the Sharma constant, S_0, is also a constant with the same characteristic value as that observed in different systems by earlier workers, and it is also independent of temperature. All other parameters estimated are temperature-dependent, and any small variation in the estimated value of the parameter can be attributed to differences in their chainlength.

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