Estimation of the Sharma Constant and Thermoacoustic Properties of Vegetable Oils

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The density and volume of four Indian edible vegetable oils, sunflower, rice bran, groundnut and coconut, and one Indian nonedible oil, castor oil, have been experimentally determined. The values obtained were used to estimate the volume expansivity α, hence the thermoacoustic parameters, such as the Sharma constant S_0, the isochoric temperature coefficient of internal pressure $\left[\frac{d\ln P_i}{d\ln T}\right]_V$, the isochoric temperature coefficient of volume expansion $\left[\frac{d\ln\alpha}{d\ln T}\right]_V$, reduced volume $\tilde{V}$, reduced compressibility $\tilde{\beta}$ and the Huggins parameter F. The results obtained show that the Sharma constant S_0 has the same characteristic value of 1.11 ± 0.01 for the five oils, thus establishing the constancy of the Sharma parameter. All the other parameters are of the expected order of magnitude; however, in all cases there is a uniform deviation at 293°K, which can be attributed to the behavior of density and volume at this temperature.

KEY WORDS: Density, Huggins parameter, isochoric temperature coefficient of internal pressure, isochoric temperature coefficient of volume expansion, physicochemical properties, reduced compressibility, reduced volume, Sharma constant, vegetable oils, volume expansivity.

In the past two or three decades, considerable importance has been given to the study of physicochemical behavior of liquid crystals in their mesophases, isotropic and crystalline phases because of various technological applications in science and industry. The liquid crystalline phase exhibits anisotropic and rheological properties of the liquid because of its peculiar existence between the solid crystalline and isotropic liquid states. The peculiarity in its structure has prompted both physicists and chemists to investigate other properties. Sharma (1-5) has recently studied the volume expansivity α and estimated various thermoacoustic parameters, including the Sharma constant, S_0, in nonmesomorphic systems such as polymers, polycrystalline solids, liquid alkali halides and ionic liquids. He found that the Sharma constant has a characteristic constant value of 1.11 ± 0.01 in all these systems. He also stated that this constant will help in understanding the molecular order and intermolecular interactions in the condensed phase.

In continuation of the studies on mesomorphic systems, the present study of thermoacoustic parameters has been undertaken on four edible vegetable oils and one nonedible oil. These parameters will elucidate the thermodynamic and rheological properties that are necessary in the design of process equipment for the oil and fatty acid industry, process piping and metering pump design, distillation and separation of fatty acids and design of storage tanks. The physical properties, such as density and viscosity, of these oils are important in their evaluation as alternatives for diesel fuels.

In the present report, the densities and volume changes with temperature of four edible vegetable oils—groundnut, sunflower, coconut and rice bran—and one nonedible oil—castor oil—have been experimentally determined. The values obtained were used to estimate the thermoacoustic parameters in the corresponding temperatures as proposed by Sharma. This is the first report of studies on the estimation of thermoacoustic parameters, as proposed by Sharma for vegetable oils.

EXPERIMENTAL PROCEDURES

Genuine oils were purchased from the following sources: castor oil (B.S.S. grade; Sanjeev Kumar Dhanji, Hyderabad, India), groundnut refined oil ("Tushar;" Tungabhadra Industries, Kurnool, India), sunflower ("Dhara;" National Dairy Development Board, Anand, India), rice bran ("Branola;" Siris Industries, Hyderabad, India) and coconut ("Parachute;" Bombay Oil Industries Pvt. Ltd., Bombay, India).

Density. Densities were measured by using a precision 10-mL corning-glass density bottle with a fine bore capillary stopper. After completely filling the bottle with the sample, the stopper is introduced gradually, until it is tightly stoppered. The weight of the stoppered density bottle with the sample is taken, and then it is immersed in a constant temperature bath maintained at +0.1°C. Julabo F-30 circulating type (Julabo, Seelbach, Germany) was used for this purpose. Ethanol was used as a circulating medium for temperatures from −30 to 30°C, whereas water was the circulating medium for temperatures beyond ambient to 353°K. The difference between the reciprocal densities at two consecutive temperatures gave the volume change between the two consecutive temperatures.

RESULTS AND DISCUSSION

The result obtained for the Sharma constant, S_0, of the five oils used in this study was compared with S_0 for polymers, alkali halides and ionic liquids observed earlier.

The Sharma constant S_0 relates the isothermal volume derivative of the intermolecular constant to the thermodynamic Gruneisen parameter and other various physical parameters, and as such it is an important parameter in investigating the physicochemical behavior of any system. As per the reports of Sharma and of Sharma and Reddy (1-5), the value of the Sharma constant is a constant for any system, either in a liquid or in a solid state. From their investigations, Sivaram and Venkatacharyulu (6) Subba Rao (7) concluded that even in the liquid state where the mesogens simultaneously exhibit the rheological properties of liquids and anisotropic properties of crystals, the Sharma constant S_0 is again a constant with the same characteristic value, 1.11 ± 0.01, as was reported by Sharma and by Sharma and Reddy (4) for certain nonmesomorphic systems. These investigators observed from their studies that S_0 assumes a lower value than the characteristic value only at and in the immediate vicinity of the transition temperatures when the system transits 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

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TABLE 1

Density and Volume of Vegetable Oils

Temperature 0°C	Sunflower oil		Rice bran oil		Groundnut oil		Coconut oil		Castor oil	
	Density gm/cc	Volume cc	Density gm/cc	Volume cc	Density gm/cc	Volume cc	Density gm/cc	Volume cc	Density gm/cc	Volume cc
−20	0.947	1.055	—	—	—	—	—	—	0.992	1.008
−10	0.940	1.063	—	—	—	—	—	—	0.986	1.014
0	0.933	1.071	0.931	1.073	0.927	1.078	—	—	0.979	1.021
10	0.926	1.079	0.924	1.081	0.920	1.086	—	—	0.972	1.028
20	0.919	1.087	0.918	1.089	0.913	1.094	0.919	1.087	0.965	1.035
30	0.918	1.088	0.916	1.090	0.912	1.095	0.917	1.089	0.964	1.036
40	0.911	1.096	0.909	1.099	0.905	1.104	0.911	1.097	0.957	1.044
50	0.904	1.104	0.903	1.107	0.898	1.112	0.904	1.105	0.950	1.051
60	0.898	1.113	0.896	1.115	0.892	1.120	0.897	1.114	0.943	1.059
70	0.891	1.121	0.889	1.124	0.885	1.129	0.897	1.114	0.937	1.067
80	0.884	1.130	0.882	1.132	0.878	1.138	0.883	1.131	0.930	1.074

or positionally) density state. Exactly at the transition temperature, S_0 drops to the lower value than at any other temperature.

In the present study, the density and volume were measured as functions of temperature (273–353°K) at intervals of 10°K. The data collected at these temperatures are presented in Table 1. The following thermoacoustic parameters have been estimated from the data on density and volume.

Isochoric temperature coefficient of internal pressure $[\frac{\mathrm{dlnP_i}}{\mathrm{dlnT}}]_{\mathrm{V}}$. To discuss the estimation of the isochoric temperature coefficient of internal pressure, it is necessary to explain the estimation of volume expansion. The volume expansivity α can be written as:

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

where $\Delta V = (V_2 - V_1)$, $\Delta T = (T_2 - T_1)$, $V_n = (V_1 + V_2)/2$, and V_2 and V_1 are molar volumes at T_2 and T_1, respectively.

Haward and Parker (8) obtained an expression for the isochoric temperature coefficient of thermal expansion:

$$\left[\frac{dlnP_i}{\Delta T}\right]_V = \frac{2}{\tilde{\beta}}\left[\frac{dln\alpha}{dlnT}\right]_V = \frac{-2 \times (1 + 2\alpha T)}{\tilde{V}^{C_1}} \qquad [2]$$

here P_i is the internal pressure, $\tilde{\beta} = \beta/\beta^*$ is the reduced compressibility and β and β^* are the compressibilities at temperature T and at absolute zero and zero pressure, respectively, V and α are the molar volume and volume expansivity at temperature T, and C_1 is the dimensionless pressure coefficient of bulk modulus. We have used this equation and estimated the various parameters. The results obtained are given in Table 2.

The isochoric temperature coefficient of internal pressure $[\frac{dln\,P_i}{dlnT}]_V$ increases with the rise in temperature for all five oils examined with a value around −0.6. However, at 293°K it has a value around −0.7. This is in agreement with the observations made by earlier investigators for compounds other than oils (1–7).

Isochoric temperature coefficient of volume expansion $[\frac{\mathrm{dln}\alpha}{\mathrm{dlnT}}]_{\mathrm{V}}$. This parameter (Table 2) was found to be −1.4 at all temperatures except 293°K, where it exhibits a slightly anomalous behavior. However, it decreases as the value of α increases, and, accordingly, it has a minimum value at 293°K where the value of α is abnormally high. These results are again in accordance with those obtained for compounds other than oils. The isochoric temperature coefficient of volume expansion can be expressed as:

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

where S^* and S_0^* are the Sharma parameters defined below.

The pressure coefficient of bulk modulus C_1, which was introduced by Moelwyn-Hughes (9) is:

$$C_1 = \left[\frac{d}{dp}\left(\frac{1}{\beta}\right)\right]_T = \left[\frac{dln\beta}{dlnV}\right]_T \qquad [4]$$

Sharma (1) obtained the compressibility expression from the reduced equation of state to estimate C_1 and calculated the values of $\tilde{\beta}$ and α according to the expressions:

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

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

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 study, α was calculated from Equation 1.

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

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

Table 2 shows that the value of $\tilde{V}$ for the five oils examined ranges from 1–1.3. The values of $\tilde{V}$ for all systems other than oils investigated by Sharma, Sharma and Reddy (1–5), Sivaram and Venkatacharyulu (6) and Subba Rao (7) were in the range of 1.0–1.412. Therefore, the values for the oils are comparable to any other nonmesomorphic and mesomorphic systems, except at 293°K.

Sharma used Equations 4, 5 and 6 to estimate C_1 in terms of only α and T:

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

TABLE 2

Thermoacoustic Properties of Vegetable Oils

Temperature °K	α $\times 10^3$ K^{-1}	$\left[\frac{dlnP_i}{dlnT}\right]_V$ 10^{-3} K^{-1}	$\left[\frac{dln\alpha}{dlnT}\right]_V$ 10^{-6} K^{-2}	$\tilde{V}$	$\tilde{\beta}$	S_0	S^*	F
Sunflower oil								
253	0.722	−0.600	−1.365	1.163	4.545	1.120	1.243	1.357
263	0.728	−0.595	−1.383	1.169	4.647	1.121	1.125	1.339
273	0.733	−0.589	−1.400	1.176	4.748	1.121	1.267	1.322
283	0.739	−0.584	−1.418	1.183	4.855	1.121	1.279	1.305
293	0.148	−0.699	−1.086	1.042	3.105	1.110	1.057	1.642
303	0.744	−0.574	−1.451	1.195	5.053	1.121	1.300	1.273
313	0.751	−0.568	−1.470	1.202	5.169	1.120	1.313	1.255
323	0.757	−0.563	−1.489	1.209	5.287	1.120	1.326	1.237
333	0.762	−0.557	−1.507	1.216	5.404	1.120	1.338	1.219
343	0.769	−0.552	−1.528	1.223	5.534	1.119	1.352	1.200
Rice bran oil								
273	0.735	−0.589	−1.401	1.176	4.756	1.121	1.267	1.321
283	0.740	−0.584	−1.419	1.183	4.859	1.121	1.279	1.304
293	0.148	−0.699	−1.087	1.042	3.107	1.110	1.058	1.641
303	0.747	−0.574	−1.452	1.196	5.061	1.121	1.301	1.272
313	0.752	−0.568	−1.471	1.202	5.173	1.120	1.314	1.254
323	0.758	−0.563	−1.490	1.209	5.292	1.120	1.326	1.236
333	0.764	−0.557	−1.509	1.216	5.412	1.120	1.339	1.121
343	0.771	−0.551	−1.529	1.224	5.540	1.119	1.352	1.199
Groundnut oil								
273	0.737	−0.589	−1.402	1.177	4.760	1.121	1.268	1.320
283	0.743	−0.583	−1.421	1.184	4.869	1.121	1.280	1.302
293	0.149	−0.699	−1.087	1.042	3.110	1.110	1.058	1.640
303	0.751	−0.573	−1.455	1.197	5.075	1.120	1.303	1.269
313	0.756	−0.567	−1.473	1.203	5.188	1.120	1.315	1.252
323	0.762	−0.562	−1.492	1.210	5.307	1.120	1.328	1.234
333	0.768	−0.556	−1.511	1.217	5.428	1.120	1.341	1.215
343	0.773	−0.551	−1.530	1.224	5.551	1.119	1.353	1.197
Coconut oil								
293	0.148	−0.699	−1.086	1.042	3.105	1.110	1.057	1.642
303	0.747	−0.574	−1.452	1.196	5.061	1.121	1.301	1.272
313	0.750	−0.568	−1.469	1.202	5.167	1.120	1.313	1.255
323	0.757	−0.563	−1.489	1.209	5.289	1.120	1.326	1.236
333	0.055	−0.720	−1.037	1.018	2.880	1.106	1.024	1.695
343	1.481	−0.434	−2.016	1.376	9.288	1.092	1.677	0.756
Castor oil								
253	0.588	−0.622	−1.297	1.135	4.165	1.119	1.198	1.424
263	0.694	−0.600	−1.365	1.162	4.543	1.120	1.243	1.357
273	0.699	−0.595	−1.381	1.169	4.638	1.121	1.254	1.341
283	0.704	−0.590	−1.398	1.175	4.736	1.121	1.265	1.324
293	0.140	−0.701	−1.082	1.040	3.086	1.110	1.055	1.646
303	0.710	−0.580	−1.430	1.187	4.927	1.121	1.287	1.293
313	0.715	−0.575	−1.447	1.194	5.030	1.121	1.298	1.277
323	0.719	−0.570	−1.464	1.200	5.236	1.121	1.309	1.260
333	0.725	−0.565	−1.483	1.207	5.250	1.121	1.322	1.242
343	0.730	−0.559	−1.501	1.214	5.364	1.120	1.334	1.225

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

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

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

and the reduced compressibility (1) is:

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

As seen in Table 2, $\tilde{\beta}$ is estimated as a function of temperature for all five oils studied at normal atmospheric pressure, and the values range from 3 to 5. The value at 293°K is lowest for all oils except for coconut oil, where the lowest value is obtained at 333°K.

The Sharma constant S_0. Sharma expressed S_0 as:

$$S_0 = -\frac{1}{2}\left(\frac{d1nP_i}{d1nT}\right)_V\left(\frac{\tilde{\alpha}}{\tilde{V}}\right) = \frac{S^*S_0^*\tilde{\alpha}}{\tilde{\beta}\,\tilde{V}}\,\frac{(1 + 2\alpha T)}{\tilde{V}^{C_1}}\,(3 + 4\alpha T) \qquad [11]$$

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

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

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

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

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

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

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

Parameter S^*. S^*, calculated for the five oils, is in the range 1.0–1.35. The values are again comparable to the values of S^* for polymers, which are in the range 1.06–1.622, for polycrystalline solids at 1.2, for alkali halides at 1.5, for ionic liquids in the range 1.179–1.644 and for liquid crystals at 1.444.

Huggins parameter F. Huggins (10,11) obtained a parameter which may be expressed in terms of temperature and pressure derivatives of compressibility as:

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

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

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

and from Expressions 9, 10, 17 and 18 that:

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

By using Equations 11–13 and 19, the Huggins parameter F can also be expressed in terms of the Sharma constant S_0 and the parameters S^* and S_0^*. All the parameters can again be expressed in terms of the single measurable parameter α.

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

By means of Equation 13, S_0 can also be expressed as:

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

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

It is evident from the above 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. We have, therefore, successfully adopted this method and obtained the various thermoacoustic parameters of the five oils reported here.

Table 2 shows that the Sharma constant S_0, which is estimated as a function of temperature in all five oils examined, is independent of temperature, but dependent on α. As the volume expansivity α increases, S_0 decreases. For all five oils studied, the volume expansivity is lower at temperature 293°K than at any other temperature, and, as a consequence of this, the Sharma constant S_0 is lower at this temperature than at any other temperature. Yet, its value is constrained to 1.11 ± 0.01, even in viscous systems such as vegetable oils.

Fats, unlike pure chemical compounds, do not melt at a fixed temperature but over a range. In this temperature range they are plastic. That is, they are soft and can be spread, but they do not flow. In other words, their properties are intermediate between those of a solid and a liquid. The distinction between an oil and a fat is simply that at ambient temperatures, oils are liquids and fats are solids. The plasticity of a fat results from its being a mixture of a number of different "triglycerides," with each triglyceride having its own melting point. When a large proportion of the triglycerides are below their melting point, the mixture is solid, and consists of a network of minute crystals surrounded by a smaller quantity of liquid triglycerides. The solid network is not rigid, however, and the crystals can slide over one another, giving rise to the plastic character of the fat. If the temperature of the fat is raised, an increasing proportion of the triglycerides melt, the solid network gradually breaks down, and the plasticity of the mixture increases until it becomes liquid when all the triglycerides have melted.

The melting points of fats are also affected by the fact that many triglycerides exist in several crystalline forms—that is, they are polymorphic. Each crystalline form has its own melting point, and when oils are cooled, mixtures of different crystalline form and, therefore, different melting points may be obtained, depending upon how the cooling was carried out.

From the results detailed above, it is concluded that the Sharma constant S_0, which is a characteristic constant in a number of different systems investigated by earlier workers, also has the same characteristic value of 1.11 ± 0.01 for the five oils examined, thus establishing the constancy of the Sharma parameter S_0. At all temperatures, S_0 is uniformly 1.12, except at 293°K, where it is uniformly 1.11 in all five oils.

All other parameters investigated for the five oils (castor, groundnut, sunflower, rice bran and coconut oils) are of the expected order of magnitude. However, again there is a uniform deviation at 293°K, as at this temperature the volume expansivity for all oils under study is much less, when compared to the same at any other temperature investigated. Because all the parameters under investigation are estimated by using only the coefficient of volume expansion α, it is not unreasonable to expect the reflection of α in the estimated parameters.

REFERENCES

1. Sharma, B.K., and R.R. Reddy, *Ind. J. Pure and Appl. Phys. 21*:396 (1985).
2. Sharma, B.K., *J. Phys. 16*:1959 (1983).

3. Sharma, B.K., *Phys. Letters 99*:227 (1983).
4. Sharma, B.K., and R.R. Reddy, *J. Poly. Matter 1*:180 (1984).
5. Sharma, B.K., *Ibid. 1*:193 (1984).
6. Sivaram, C., and P. Venkatacharyulu, *Crys. Res. Technol. 25*:939 (1990).
7. Subba Rao, V., Master's Thesis, Nagarjuna University, India, 1981.
8. Haward, R.N., and B.M. Parker, *J. Phys. Chem. 72*:1842 (1968).
9. Moelwyn-Hughes, E.A., *Ibid. 55*:1246 (1951).
10. Huggins, M.L., *J. Chem. Phys. 5*:143 (1937).
11. Huggins, M.L., *Ibid. 15*:212 (1947).

[Received September 23, 1993; accepted February 9, 1994]