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Thermal expansivity coefficient (α) and isothermal bulk modulus (K_T) obtained for fatty acids in liquid phase to estimate the Anderson-Grüneisen parameter (δ_T)

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Abstract

Background: A conceptual equation to evaluate the Anderson–Grüneisen parameter (δ_T) has been used. This equation has been applied to estimate the parameter for the fatty acids with long carbon chain.

Methods: For predicting the values of density (molar volume), volume thermal expansivity under isothermal condition and bulk modulus, it was used two cubic equation of state for the liquid phase. Peng-Robinson (P-R) was the one chosen to represent density behavior in accordance with the scarce experimental data for comparison.

Results: For the three acids, Lauric, Palmitic and Stearic, Anderson–Grüneisen parameter was calculated, in two range of pressures (1-10atm; 30-50atm) and in a range of temperature of 350-450 K.

Conclusion: Despite there are no experimental data available in the literature, these results are found to be consistent with the thermodynamic constraints.

Keywords: volume thermal expansivity, bulk modulus, liquid and solid phase, anderson-grüneisen parameter, peng-robinson equation

1. Introduction

It is widely known that any equation of state (EoS) or thermodynamic formulation must satisfy the boundary conditions at zero pressure and infinite pressure. Analyses of the behavior of materials at extreme compression have been very useful for deriving some thermodynamic constraints which provide a critical test of different theories. The infinite-pressure parameters determined through extrapolation by considering a material to remain in the same phase when compressed to the extreme limit ($V \rightarrow 0$), V being the volume of the material, are equally important as the zero-pressure parameters for predicting the properties of materials in the observed range of finite pressures with the help of an EoS (Equation of State). It is true that no material can exist at extreme compression ($V \rightarrow 0$), and some materials with a particular phase do not exist even at zero pressure or atmospheric pressure: they exist only for a given range of finite pressures. But the extrapolated values of parameters in the limit of infinite pressure provide a fine and powerful control on the properties to be determined in the observed range of pressures.

Kumar *et al.*, 2015 [1] have analysed the thermodynamic properties in the limit of infinite pressure. A number of thermodynamic infinite pressure limits have been used to establish that isothermal and adiabatic properties become identical at extreme compression. It has been found that isobaric heat capacity (C_P) equals to isochoric heat capacity (C_V). Bulk or Rigidity modulus under isotherm and adiabatic conditions remains the same. Also, the ratio of isothermal and adiabatic Anderson-Grüneisen parameters remains finite in the limit of infinite pressure.

In the present paper, an appropriate equation of state was confirmed to be used and then volume thermal expansivity and the isothermal bulk modulus for fatty acids (C_{14}-C_{18}), under isothermal conditions, were estimated. Also, an interpretation for isothermal Anderson–Grüneisen parameter is made. To check the validity, present expressions are applied for three fatty acids with long carbon chain. The development of formulation is shown in Section 2 and results are discussed in Section 3. Knowledge of δ_T (p, T) is important to find the high P-high T behavior of a number of important properties in thermal physics, including entropy, thermal expansivity, thermal pressure and the Grüneisen parameter (γ).

2. Method of analysis

The parameter δ_T is a dimensionless thermoelastic parameter important in thermodynamic studies involving high temperature at high pressure. A brief history of attempts to define δ_T in terms of fundamental interatomic potentials has been given [2]. As experimental measures demand high costs, calculations provide a way to find δ_T, since it is possible to find it using equation of state. This methodology can be demonstrated for some fatty acids, where δ_T is calculated over a considerable range of (p, T) field. For other materials, it was found that δ_T decreases at high compression, but is independent of temperature [2].

The isothermal Anderson–Grüneisen parameter δ_T is defined as [3].

$$\delta_T = \frac{-1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_p \tag{1}$$

Where α is the thermal expansion coefficient and K_T is the isothermal bulk modulus. Using the following thermodynamic identity [3].

$$K_T\left(\frac{\partial \alpha}{\partial p}\right)_T = \frac{1}{K_T}\left(\frac{\partial K_T}{\partial T}\right)_p \tag{2}$$

Combining Eq. (1), and the isothermal bulk modulus definition formulation

$$K_T = -V\left(\frac{\partial p}{\partial V}\right)_T, \tag{3}$$

Then, the Anderson-Grüneisen parameter δ_T may be also written as

$$\delta_T = \frac{-V}{\alpha}\left(\frac{\partial \alpha}{\partial V}\right)_T \tag{4}$$

Equation (4) has been applied to the systems such as H_2, D_2, NaCl, and MgO at relatively low pressure, the calculated values [4] of the isothermal bulk modulus was found to be in agreement with available experimental data in the pressure range.

Also, Eq. (4) is generally used to calculate the Anderson-Grüneisen parameter δ_T(T,P) of liquids extended to solids, which has a need to obtain the values of α, V and $\left(\frac{\partial \alpha}{\partial V}\right)$. In this work, all the values are obtained by calculating using the results from Peng-Robinson equation of state, with the help of Eq. (8) for fatty acids cited above at temperatures of 300-450 K. Up to now, there are no experimental data reported by any researcher based on the theoretical or experimental measurement of thermodynamic properties at high pressure.

3. Results and Discussion

Table 1 illustrates the equations of state used in this work. In order to choose and test the validity of them, P-R or vdW [5], and select the one to be used in the calculations. The values of the liquid molar volume (V, cm^3/mol), the isothermal bulk modulus (K_T) and the thermal expansion coefficient α (T,P) (K^{-1}) were determined.

Table 1: Cubic Equations of State used in this work and the derivatives.

	Van der Waals	**Peng-Robinson**
pVT	$p = \frac{RT}{V-b} - \frac{a}{V^2}$	$p = \frac{RT}{V-b} - \frac{a}{V^2 - 2Vb - b^2}$
A	$27R^2 \frac{T_c^2}{64p_c}$	$a = 0.45724R^2\alpha\frac{T_c^2}{p_c}$
B	$\frac{RT_c}{8p_c}$	$b = 0.07780R\ \frac{T_c}{p_c}$
α	--	$\alpha = \left[1 + (0.37464 + 1.54336\omega - 0.26992\omega^2)\left(1 - \left(\frac{T}{T_c}\right)^{0.5}\right)\right]^2$
$\left(\frac{\partial P}{\partial T}\right)_V$	$\frac{R}{V-b}$	$\frac{R}{V-b} - \frac{da/dT}{V^2 - 2Vb - b^2}$
$\left(\frac{\partial P}{\partial V}\right)_T$	$-\frac{RT}{(V-b)^2} + \frac{2a}{V^2}$	$-\frac{RT}{(V-b)^3} + \frac{2a(T)[V-b]}{(V^2 - 2bV - b^2)^2}$
$\left(\frac{\partial V}{\partial T}\right)_p$	$\frac{-RV^4 + RbV^3}{2a(V-b)^2 - RTV^3}$	$\frac{-\frac{R}{V-b} + \frac{da/dT}{V^2 + 2Vb - b^2}}{-\frac{RT}{(V-b)^3} + \frac{2a(T)[V-b]}{(V^2 - 2bV - b^2)^2}}$

The derivatives developed and used in the programs to obtain the thermal parameters are highlighted in Table 1. To estimate the derivative of da/dT by considering that for P-R equation the parameter "a" is given by:

$$a = 0.45724R^2\alpha\frac{T_c^2}{p_c} = (A_1).\propto = (A_1).\left[1 + W_1.\left(1 - \left(\frac{T}{T_c}\right)^{0.5}\right)\ \right]^2 \tag{5}$$

and

$$W_1 = 1 + (0.37464 + 1.54336\omega - 0.26992\omega^2) \tag{6}$$

Then

$$\frac{da}{dT} = \frac{-A_1W_1}{(TT_c)^{0.5}}.\left[1 + W_1.\left(1 - \left(\frac{T}{T_c}\right)^{0.5}\right)\right] \tag{7}$$

In this work, fatty acids were chosen as systems to be tested. Fortunately there exists a considerable body of published information and this one will be utilized in the future work to investigate whether symmetry exerts any systematic effects by examining one to one comparisons of structural isomers. Data was taken from two large databases of melting points, enthalpies of fusion and temperatures of organic compounds [6, 7].

Table 2 shows the physico-chemical properties of the compounds [5] such as critical pressure and temperature (p_c, t_c), acentric factor (ω), normal boiling temperature (T_{eb}), temperature and pressure in the triple point (T_{tp}, P_{tp}) and molar volume in the solid phase (V_S, cm^3mol^{-1}).

Table 2: Properties for the chemicals.

I	p_c/atm	t_c/K	Ω	T_{eb}/K	T_{trp}/K	P_{ptr}/bar	$V_S^{20^oC}$
Caprylic acid $C_8H_{16}O_2$	28.69	693.00	0.734	510.00	289.66	–	--
Capric acid $C_{10}H_{20}O_2$	21.00	726.00	0.749	530.00	304.55	9.732E-07	--
Lauric acid $C_{12}H_{24}O_2$	18.68	743.43	1.000	571.00	316.98	–	198.61
Myristic acid $C_{14}H_{28}O_2$	16.44	765.19	1.000	523.20	327.32	2.134E-07	--
Palmitic acid $C_{16}H_{32}O_2$	14.68	785.22	0.999	612.15	335.66	8.266E-08	258.85
Stearic acid $C_{18}H_{36}O_2$	13.26	805.09	1.018	634.20	342.49	4.266E-08	282.03

In order to reduce complications, only rigid molecules were considered, i.e. those not possessing, for example, flexible methylene chains that would be expected to take up multiple conformations in the liquid state that are not seen in the solid.

In addition, compounds with groups that might engage in H-bonding such as hydroxyls, combinations of amino with nitro, etc. were excluded. This was done to avoid any disruption to the symmetry effect that might occur from intermolecular interactions in either the solid or liquid states.

The density results obtained from P-R Equation using the values given in Table 1 and 2 are reported in Table 3 along with the input data on experimental density. For the sake of comparison, the calculated results presented by Lauric, Palmitic and stearic acids are also listed in Table 3.

Table 3: Thermophysical properties of fatty acids [8-13]. (S : solid; L: Liquid)

Name Chemical Formula	T_f (^0C)	✍H_f (kJ/kg)	ρ (kg/m^3) (ref)	ρ (kg/m^3) this work (P-R)
Caprylic acid $C_8H_{16}O_2$	16.3	148	901[7-12]	Not available
Capric acid $C_{10}H_{20}O_2$	32	152.7	878[7-12].	Not available
Lauric acid $C_{12}H_{24}O_2$	42–44	178	1007[7-12](S),862(L)	847-938 (L)
	24	-	1007(S)[1a,22a,24a]	1000.3(S)*
	40	-	909(S)[25a]	1005.9(S)*
	22	-	930±20(S)[26a]	997.7(S)*
Myristic acid $C_{14}H_{28}O_2$	52.2–58	182.6–199	862.2	Not available
Palmitic acid $C_{16}H_{32}O_2$	57.8–61.8	185.4	850(L),989(S)	802-853(L)
Stearic acid $C_{18}H_{36}O_2$	41–43	211.6	862(L)1007(S)	600-687 (L)

Legend: H: Latent heat (kJ/kg), Tm: Melting temperature (^0C). ρ: Density (kg/m^3) * calculated using α – parameter from P-R for liquid phase.

It was not published in Table 2, however van de Waals equation was also used to obtain the density for Lauric, Palmitic and Stearic acid at the respective fusion point condition. The findings show that the value remained practically unchanged, and respectively, are 662, 618 and 611 $kg.m^{-3}$. As far as this point is concerned, P-R equation is really much better. Then, As we can see in Table 3, acids such as Lauric, Myristic and Palmitic are good examples to be used for Eq. (8) estimatives in the suitable pressure and temperature range.

Volume thermal expansivity (α) is a very important parameter to study thermodynamic and thermoelastic properties for solids and liquids in general. It is a tedious work to measure the value of volume thermal expansivity in laboratories, so various theoretical attempts [14-19] have been made to solve this problem.

From Tables A1 – A6 (in Appendix A), we can see that the calculated values of the thermal expansion coefficient α (T, P) using both EoS are not in good agreement in the whole pressure range, which demonstrates that it was recommend the validition of Peng-Robinson Equation. Figures 1-3 are shown the behavior of bulk modulus (K_T) as a function of the pressure for the three acids used in this work.

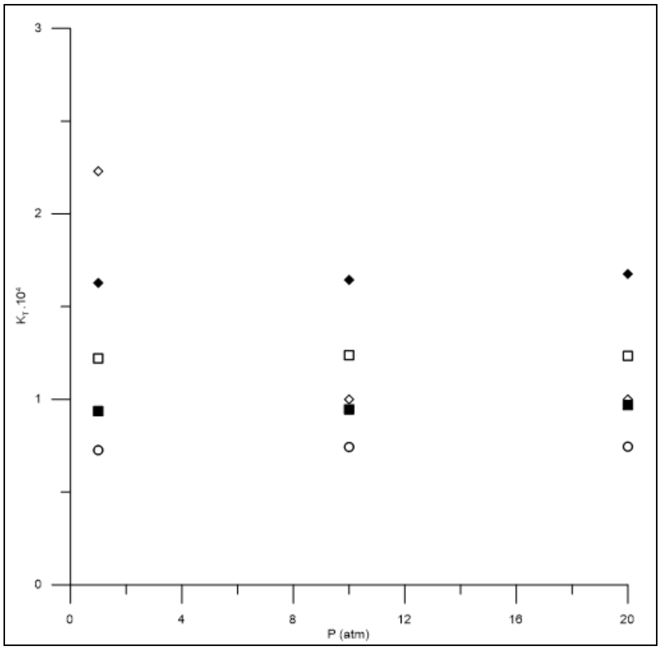

Fig 1: K_T for Stearic acid as a function of the pressure. (♦350 K, ◊400K, ☎450, ■500K, ○550K)

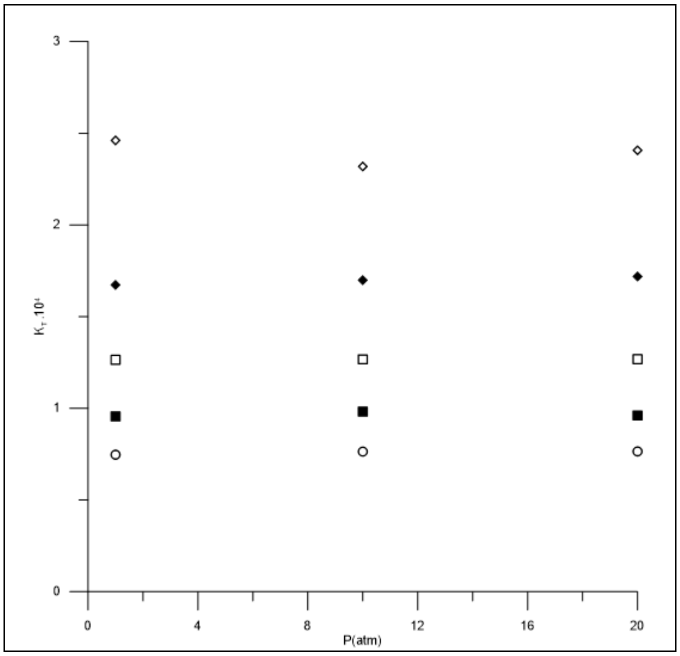

Fig 2: K_T for Palmitic acid as a function of the pressure.. (♦350 K, ◊400K, ☎450, ■500K, ○550K)

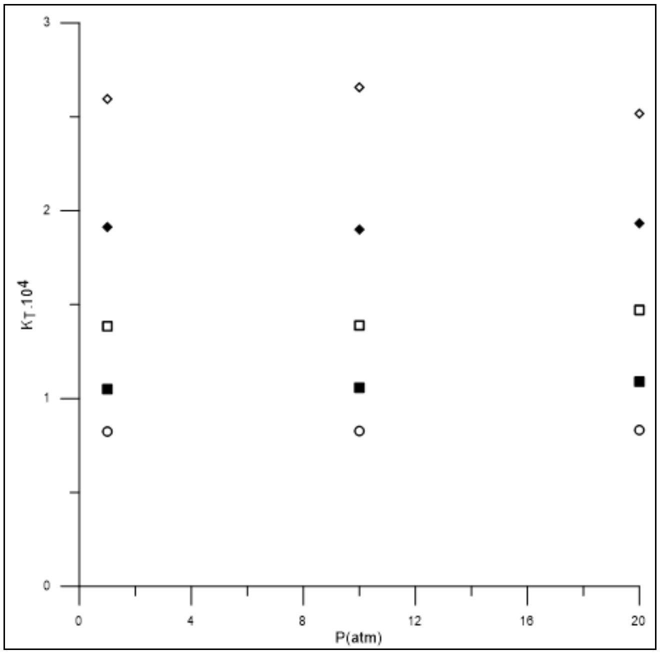

Fig 3: K_T for Lauric acid as a function of the pressure.. (♦350 K, ◊400K, ☎450, ■500K, ○550K)

As the carbon chain decreases, the effect of temperature in the bulk modulus is higher. In general, pressure effect is sligthly observed. Apart from Stearic acid at 400K, it is noted that K_T remained almost constant in the range of pressure studied. As the temperature increases, the K_T value decreases. This was observed in most of the cases studied. Acording to Mao *et al.*,2015 [20] although K_S (adiabatic bulk moduli) increases almost linearly with pressure, at 300 K exhibits a downward trend with pressure due to the softening of the shear moduli. Increasing temperature at a given pressure decreases all of the elastic moduli. In general, most of the elastic moduli exhibit similar pressure dependence at the investigated temperature range.

Table 4: Anderson-Grüneisen parameters (δ_T, mol^2/K^{2}m^6) estimated using data calculated in this work.

Name	T (K)	δ_T	δ_T
		1-10 atm	**30-50 atm**
Lauric acid	350	41.56	56.13
	400	75.93	57.28
	450	----	69.07
Palmitic acid	350	28.45	24.57
	400	31.58	29.14
	450	30.80	38.96
Stearic acid	350	18.80	17.30
	400	22.18	20.35
	450	20.32	23.45

The values of δ_T have been predicted through Eq. (8), by taking all input parameters from Tables A1-A6 (Appendix A) and Figs 1-3 for three different fatty acids. The results are shown in Table 4 as a function of temperature in two ranges of pressure.

For a given temperature, δ_T increases as the carbon chain decreases. By comparing the results, in the two pressure ranges of Table 4, it can be seen that the δ_T value remains practically unchanged. To date thaere are no experimental data that can finally confirm the application of the P-R equation as predictive of δ_T.

4. Conclusions

Peng-Robinson equation of state was approved to represent the pVT behavior for at least three fatty acids such as: Lauric, Palmitic and Stearic. Based on this finding, the coefficients of expansivity and bulk modulus were estimated and their results applied to calculate the Anderson-Grüneisen parameter.

Results have shown that similarly to other materials the estimated parameter is unchanged with temperature but have considerable influences with the carbon long chain.

5. Conflicts of Interest.

"The authors declare no conflict of interest."

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