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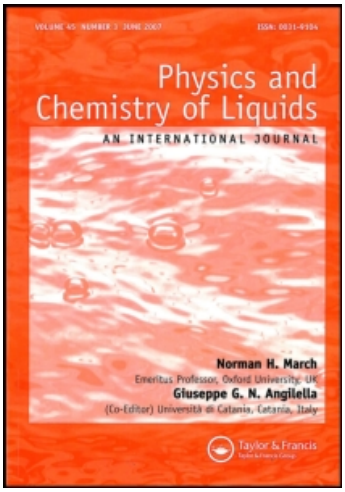

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Thermo-elastic and thermodynamic properties of light and heavy crude oil

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Thermo-elastic and thermodynamic properties of light and heavy crude oil

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Three different experiments, *viz*., ultrasound interferometry, differential scanning calorimetry, and density measurements were carried out over a wide range of temperature varying from 20°C to 70°C in light, heavy, and a mixture of light and heavy crude oil samples which differ considerably in its American Petroleum Institute gravity. The properties of the mixture have been discussed in terms of its deviation from the ideal values of mixing. The directly measured quantities such as the compression wave velocity, the specific heat at constant pressure, and the density were used to evaluate the temperature dependence of adiabatic compressibility, coefficient of volume expansion and the acoustic impedance. A correlation between thermo-elastic and thermodynamic functions of crude oils has been investigated. In particular, the ratio of the specific heats has been determined by making use of the thermo-elastic functions, which was further used to estimate the specific heat at constant volume. The values of the isothermal compressibility and the coefficient of volume expansion are used to evaluate the pressure–temperature dependence of crude oil conforming to *in-situ* reservoir conditions.

Keywords: Ultrasound velocity; Specific heats; Compressibility; Equation of state

1. Introduction

The determination of physical and thermodynamic properties of a particular crude oil is important to provide a basis for further investigations related to exploration and transportation. It plays an important role in crude oil processing such as refining operations, optimization of equipment design and *in-situ* reservoir simulation. Explorers and producers depend on the basic parameters like density, ultrasound velocity, and thermo-elastic functions like volume expansion coefficient, compressibility, equation of state and acoustic impedance, and the specific heat. Such information is also useful to enhance the recovery of crude oil from deep reservoir. Acoustic

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measurements [1–4] are favorable for the *in-situ* characterization of reservoir fluids. For want of actual information, usually oversimplified values of thermo-physical properties of hydrocarbon fluids are taken into consideration.

In the present work, laboratory experiments based on ultrasound interferometer, thermal analysis by differential scanning calorimeter and density measurements are used to derive various thermo-elastic properties of crude oil as a function of temperature. Crude oil samples which differ considerably in their American Petroleum Institute (API) gravity were procured from two different oil fields of Yibal and Mukaiznah, both located in the north of the Sultanate of Oman. To investigate the change in properties on mixing of light and heavy crude oils, a mixture of 50 : 50 composition by weight is prepared and investigated. The directly measured properties of the mixture are discussed in terms of its variation from ideal value of the mixture.

The velocity of propagation of the compression wave in crude oil was measured as a function of temperature with an ultrasound interferometer whereas the density at the corresponding temperature was determined using *Anton Paar* density meter. In order to connect the thermodynamic functions to elastic and other physical properties, the ratio of specific heats, γ $(=C_p/C_\Omega, C_p$ and C_Ω specific heats at constant pressure and constant volume) plays a vital role [5,6]. For example, if C_p and adiabatic compressibility (κ_s) are experimentally known one can easily infer C_Ω and the isothermal compressibility (κ_T) provided reliable values of γ are known. The knowledge of γ is also required in many fluid equations such as equations relating to pressure, temperature, and volume during a simple compression and expansion process. It is widely used [7] in all the equations for isentropic flows and shock waves. We are therefore suggesting that the value of γ can be determined using an exact thermodynamic equation where C_p, κ_s and the coefficient of volume expansion (β) occur as ingredients which we determine in our laboratory.

The article is subdivided into several sections. The fist section is devoted to experimental methods and results of ultrasound velocity, specific heat at constant pressure and density measured as a function of temperature for two samples of crude oil and their mixture. In the next section we discuss the thermo-elastic properties in terms of the coefficient of volume expansion, adiabatic compressibility and acoustic impedance. This is followed by a section which establishes a correlation between thermodynamic and thermo-elastic functions. Isothermal compressibility and specific heat at constant volume are discussed in the next section. Further to this we have discussed the pressure–temperature dependence of reservoir liquids in a given well. Summary and conclusions are given at the end of the article.

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2. Experimental techniques and results

2.1. *Samples of crude oils*

Crude oil is commonly classified [8] as light, medium, or heavy referring to its gravity as measured on the API scale. The API gravity is measured in degrees and is calculated using the formula, API gravity $= (141.5/\rho) - 131.5$, where ρ is the density of crude oil (in g cm^{-3}) at a temperature $t = 15.6^\circ$C. Light crude oil is defined as having API gravity higher than 31.1°, medium oil as having API gravity between 22.3 and 31.1°, and heavy oil as having API gravity below 22.3°.

The crude oil samples used in the present investigation are procured from Yibal and Mukaiznah fields, both located in the north of the Sultanate of Oman. We have used our density data (given in a later section) to measure the API for our samples. The API gravity of our samples are:

Sample-1(*Yibal*): 37.7°API
Sample-2(*Mukaiznah*): 16.6°API.

Sample-1 is classified as light and sample-2 as heavy crude oil.

To investigate the change of properties due to mixing of light and heavy crude oils, we prepared a 50 : 50 by weight mixture from the light and heavy crude oils. The heavy and light oils mix readily and form a homogeneous mixture. We used our measured density to determine the API gravity of the mixture:

Mixture of light and heavy crude oil: 26.6°API.

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As per specifications discussed earlier, the mixture falls under the category of medium oil. It should be noted that the API of the mixture, i.e., 26.6 is quite close to the average value of 27.2 of light and heavy oils. On mixing, the experimentally determined API of the mixture do not differ considerably from the ideal value of the mixture.

2.2. *Ultrasound velocity*

Velocity of compression wave, $V_L(T)$, was measured as a function of temperature by using an ultrasound interferometer, which consists of (i) a high frequency generator and (ii) the measuring cell. The high frequency generator excites the quartz crystal to generate an ultrasonic wave of frequency, $f = 5$ MHz, which propagates through the experimental liquid. The acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and the anode current of the generator becomes a maximum. If the distance is now increased or decreased and the variation is exactly half wavelength ($\lambda/2$) or multiple of it, the anode current becomes a maximum. Its position is noted using the micrometer attached to it. From the known distance, d, the wavelength (λ) of the ultrasonic wave is calculated using the relation, $d = n(\lambda/2)$, where n refers to the number of maxima over a distance d. The wavelength λ is now used to determine the velocity, $V = f\lambda$, of the ultrasonic wave in the crude oil sample. The measuring cell is specially designed to control the temperature of the experimental liquid at a desired temperature. The temperature of the cell was controlled to ± 0.1°C using a circulation thermostat (*Haake*, D8), and the accuracy of the velocity measurement stands as $\pm 1\ \mathrm{m\,s^{-1}}$.

The measured velocity as a function of temperature for the two samples and their mixture is given in figure 1. The velocity decreases linearly with temperature in all samples. The dependence of velocity on temperature can be expressed by the general relation,

$$V(t) = Vr + \Lambda_V(t - t_r) \tag{1}$$

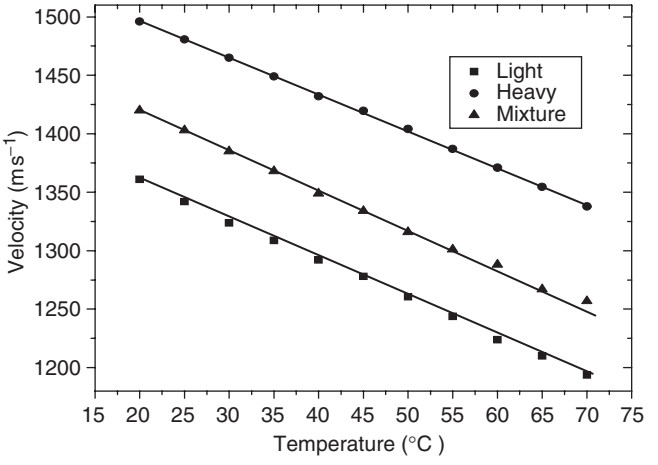

Figure 1. Variation of compression wave velocities of the crude oil.

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where $\Lambda_v = (\partial V/\partial t)$ is the temperature gradient of velocity. V_r is the reference velocity at room temperature, $t_r = 20^{\circ}$C. Explicitly, for three different samples, the temperature dependence of V (m s^{-1}) can be expressed as

$$V(t) = 1425 - 3.327(t - t_r) \quad \text{(Light)} \tag{2a}$$

$$V(t) = 1559 - 3.151(t - t_r) \quad \text{(Heavy)} \tag{2b}$$

$$V(t) = 1484 - 3.304(t - t_r) \quad \text{(Mixure)}. \tag{2c}$$

The velocity of sound in heavy oil at room temperature is found to be higher than the mixture and light oil. The velocity in heavy oil is higher by more than 9% than that of the light oil. However we may recall that the light and heavy oils differ in their API gravity by more than 17%. It is not only the density, but other atomistic features like inter-atomic forces and microscopic structure also control the propagation of compression wave through liquid hydrocarbons. The propagation of compression wave largely depends on internal molecular dynamics of the sample. The atomistic theory [9] suggests that the velocity of propagation of elastic wave in polyatomic molecules depends on force constant, molecular mass of the constituent species, and the distance between these molecules.

It may be noted that the velocity of compression wave in the mixture is very close to the ideal value, i.e., $V_{\text{mix}}^{\text{ideal}} = \sum x_i V_i^{\circ}$, where x_i is the composition fraction and V_i° is the velocity of the components. For example, the measured value of V_{mix} at 20°C has been found as 1420 m s^{-1} which is slightly less than the ideal value, $V_{\text{mix}}^{\text{ideal}} = 1428.5$ m s^{-1}. Similar trend for the measured velocity in the mixture also has been observed by Wang and Nur [10].

2.3. *Specific heat at constant pressure*

The specific heat at constant pressure (C_p) at different temperatures was measured using a differential scanning calorimeter (DSC Q10, TA Instruments, New Castle, Delaware). The instrument was calibrated for heat flow and temperature using *n*-hexane

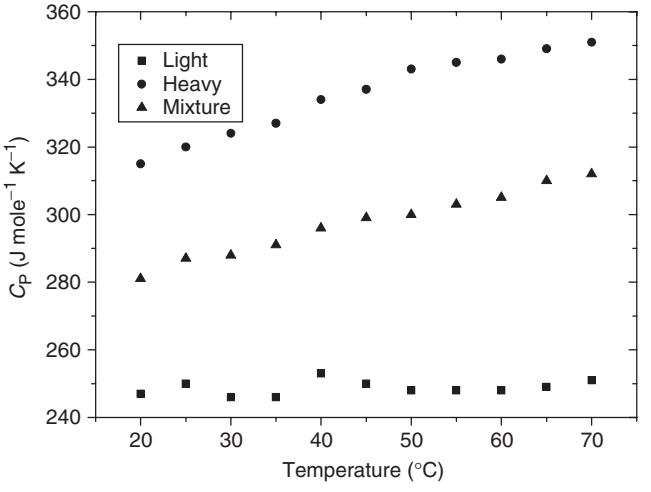

Figure 2. Variation of specific heat at constant pressure (C_P) with temperature for light, heavy, and mixture of crude oils.

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(m.p. -94°C; $\Delta H_m = 151\,J\,g^{-1}$), distilled water (m.p. 0°C; $\Delta H_m = 334\,J\,g^{-1}$) and indium (m.p. 156.5°C; $\Delta H_m = 28.5\,J\,g^{-1}$). Standard deviation was used to identify the variability or error in the experimental measurements.

The values of C_P determined at different temperatures for light, heavy and the mixture of crude oils are plotted in figure 2. At $t = 20^{\circ}$C, C_p for heavy oil ($315\,J\,mol^{-1}\,K^{-1}$) is about 27% higher than that of the light oil ($247\,J\,mol^{-1}\,K^{-1}$). The difference grows with increasing temperature to become 40% larger at $t = 70^{\circ}$C. At low temperature C_P of the mixture is found to be very close to the average value. It may be noted that the value of C_P for crude oils are very high, nearly equal to $40R$. This is a characteristic feature of the complex organic liquids. Some of the other complex organic liquids such as *n*-octane also exhibit very high C_P of the order of $32R$ [11].

The temperature dependence of C_P for light and heavy oils is quite in contrast to each other. C_P of heavy oil is found to increase almost linearly with temperature whereas for light oil it exhibits little or no temperature-dependence. The 50 : 50 mixture of light and heavy oil also shows a linear temperature-dependence of C_P, unlike the light oil.

2.4. *Temperature dependent density*

The density of the samples was measured using *Anton Paar* density meter (DMA 5000). The unit consists of a U-shaped oscillating tube and a system for electronic excitation, frequency counting, and display. The injected sample volume is kept constant and vibrated. The density is calculated based on a measurement of sample oscillation period and temperature. The temperature was controlled $\pm 0.01^{\circ}$C during the measurement using a built-in thermostat. By measuring the damping of the U-tube's oscillations caused by the viscosity of the filled-in sample, the instrument automatically corrects the viscosity related errors. The above instrument enables density to be measured to an accuracy of $\pm 5 \times 10^{-3}\,kg\,m^{-3}$.

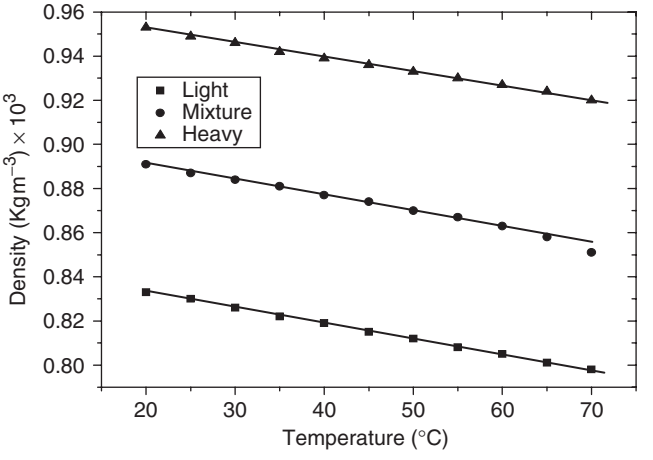

Figure 3. Variation of density with temperature for the crude oil samples.

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The density of the light and heavy crude oils and their mixture was measured as a function of temperature ranging from 20 to 70°C. The densities are found to be linearly decreasing with increasing temperature (figure 3) which can be represented by the general expression,

$$\rho(t) = \rho_{\mathrm{r}} + \Lambda_{\rho}(t - t_{\mathrm{r}}) \tag{3}$$

where $\Lambda_{\rho} = (\partial\rho/\partial t)$, is the temperature gradient of density in (kg m^{-3} C^{-1}) at atmospheric pressure, t_{r} is the room temperature (20°C) and ρ_{r} is the density at room temperature. The following equations describe the dependence of density on temperature for the three samples,

$$\rho(t) = 847.015 - 0.7007t \quad \text{(Light)} \tag{4a}$$

$$\rho(t) = 965.522 - 0.6470t \quad \text{(Heavy)} \tag{4b}$$

$$\rho(t) = 906.728 - 0.7514t \quad \text{(Mixture)}. \tag{4c}$$

The results suggest that the density of heavy oil at room temperature is about 14% higher than that of light crude oil. For the mixture the density at room temperature is 891.7 kg m^{-3} which is very close to the ideal value $\rho_{\mathrm{ideal}}^{\mathrm{mix}} = \sum x_i \rho_{\mathrm{i}}^{\mathrm{o}} = 892.8\,\mathrm{kg\,m^{-3}}$ where ρ_i^{o} is the density of the components. However, the temperature gradient of density, Λ_{ρ} in the mixture is higher than those of light and heavy oil by 7 and 14% respectively.

3. Analysis of thermo-elastic properties

3.1. *Coefficient of volume expansion*

The coefficient of volume expansion (β) is an important thermo-physical function for liquid hydrocarbons which evaluates its expansion on heating. Most of the liquids exhibit positive volume expansion except liquid water between 0 and 4°C where it undergoes a negative expansion coefficient. Many other substances [12] are also found

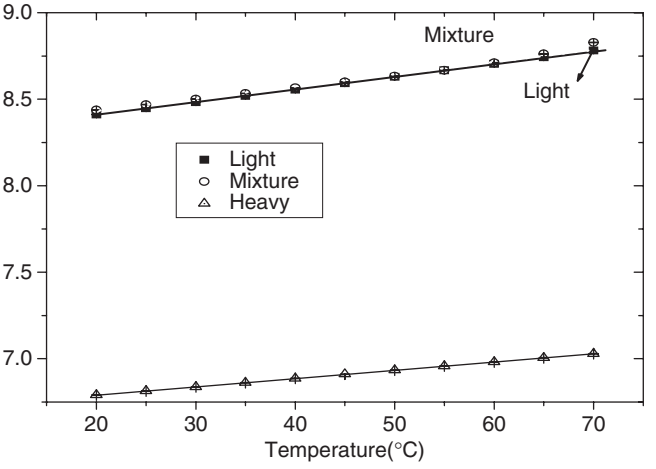

Figure 4. Coefficient of volume expansion (β) *vs.* the temperature forlight, heavy, and mixture of crude oils.

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to show negative expansion coefficient. We have used our measured values of temperature-dependent density, $\rho(t)$, to evaluate β,

$$\beta = \frac{1}{\Omega}\left(\frac{\partial \Omega}{\partial T}\right)_{\mathrm{P}} = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_{\mathrm{P}} \tag{5}$$

where Ω is the volume. For the range of temperature of our measurement, the computed values of β for light, heavy, and the mixture can be represented as,

$$\beta(t) = (8.2753 + 0.00743t) \times 10^{-4}\,\mathrm{C}^{-1} \quad \text{(Light)} \tag{6a}$$

$$\beta(t) = (6.6951 + 0.00477t) \times 10^{-4}\,\mathrm{C}^{-1} \quad \text{(Heavy)} \tag{6b}$$

$$\beta(t) = (8.2617 + 0.00738t) \times 10^{-4}\,\mathrm{C}^{-1} \quad \text{(Mixture)} \tag{6c}$$

β as a function of temperature is plotted in Figure 4. β for light oil is about 24% higher than that of heavy oil. Interestingly, β for the mixture is found to be very close to that of the light oil though they differ from one another in ρ and $(\partial\rho/\partial t)$. The larger gradient of $(\partial\rho/\partial t)$ for mixture is compensated by its larger value of ρ and therefore we finally have obtained a closer value of β for both light oil and the mixture.

β for all the three samples increases linearly with temperature. $(\partial\beta/\partial t)$ for light oil and the mixture is almost 55% higher than the heavy oil. Obviously the crude oils with high API are likely to expand more rapidly in comparison to oils with less API gravity.

3.2. *Adiabatic compressibility*

In most of the mathematical modeling of crude oil, density, volume expansion, and the compressibility are the explicit fluid parameters which are often required.

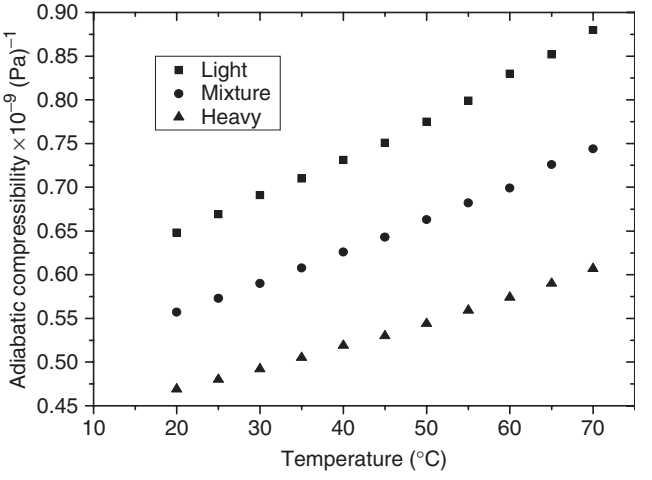

Figure 5. The adiabatic compressibility *vs.* temperature for light, heavy, and mixture of crude oils.

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An ultrasound wave, traveling with a velocity V is directly related to the adiabatic compressibility, κ_s, by the relation,

$$\kappa_s(t) = -\frac{1}{\Omega}\left(\frac{\partial\Omega}{\partial P}\right)_S = V^{-2}(t)\rho^{-1}(t). \tag{7}$$

Both quantities on the right hand side have been measured as a function of temperature and are used to compute the values of the adiabatic compressibility. The estimated values of the adiabatic compressibility are plotted in figure 5. κ_s for all samples increases with increasing temperature. Unlike density and velocity, the dependence of κ_s is not linear with temperature which can be represented by the equation,

$$k_s(t) = (5.8385 + 0.02923t + 1.86946 \times 10^{-4}t^2) \times 10^{-10} \quad \text{(Light)} \tag{8a}$$

$$k_s(t) = (4.3019 + 0.01724t + 1.13287 \times 10^{-4}t^2) \times 10^{-10} \quad \text{(Heavy)} \tag{8b}$$

$$k_s(t) = (4.9941 + 0.02649t + 1.21678 \times 10^{-4}t^2) \times 10^{-10} \quad \text{(Mixture)} \tag{8c}$$

κ_s of light oil is about 30% higher than that of heavy oil near the room temperature. The increase with temperature for the light oil is also found to be higher than other samples. For a rise of temperature from 20–70°C, κ_s for light oil increases by about 36% whereas it increases by about 28% for heavy oil.

It is also of interest to compare the values of κ_s directly determined from measured values of density and velocity in the mixture of 50 : 50 composition of light and heavy oil to those obtained from theory. For a mixture which do not experience any volume contraction or expansion on mixing the compressibility [13] can be expressed as

$$\kappa_s = \frac{\sum_i x_i \kappa_s^i \Omega^i}{\sum_i x_i \Omega^i} \tag{9}$$

where x_i is the composition fraction, where κ_s^i and Ω^i are compressibility and volume respectively of component i. For ideal mixing condition $\Omega^1 = \Omega^2$, one has $\kappa_s = \sum_i x_i \kappa_s^i$. On substituting the measured values of κ_s^i for light and heavy oil at room temperature we get κ_s (mixture) $= 5.58 \times 10^{-10}\,\mathrm{Pa}^{-1}$ which is very close to the experimentally obtained value $5.57 \times 10^{-10}\,\mathrm{Pa}^{-1}$. At a higher temperature, $t = 70^{\circ}\mathrm{C}$, the experimentally determined value of $\kappa_s = 7.44 \times 10^{-10}\,\mathrm{Pa}^{-1}$ agrees very well to that obtained theoretically ($\kappa_s = 7.435 \times 10^{-10}\,\mathrm{Pa}^{-1}$).

3.3. *Acoustic impedance*

Acoustic impedance of a fluid is analogous to electrical systems. In liquids the motion of a fluid particle is equivalent to the behaviour of electrical current in an electrical circuit having inductance, capacitance, and resistance. The electrical analogue of the pressure difference across an acoustic element of a fluid is the voltage across the corresponding part of the electrical circuit. The measured values of the velocity of sound (V) and density (ρ) can readily be used to determine the acoustic impedance (Z) in liquids,

$$Z(t) = V(t)\rho(t). \tag{10}$$

The temperature-dependent data for V and ρ are used to determine Z as a function of temperature (figure 6). The acoustic impedance of all three samples decreases linearly with temperature. The data is found to follow the equation,

$$Z(t) = Z_r + \Lambda_Z(t - t_r) \tag{11}$$

where Z_r is the acoustic impedance at t_r and $\Lambda_z = (\partial Z/\partial t)$, the temperature gradient of acoustic impedance. The temperature dependence of the acoustic impedance for the three samples can be represented by the equation,

$$Z(t) = [12.032 - 0.036(t - t_r)] \times 10^5 \quad \text{(Light)} \tag{12a}$$

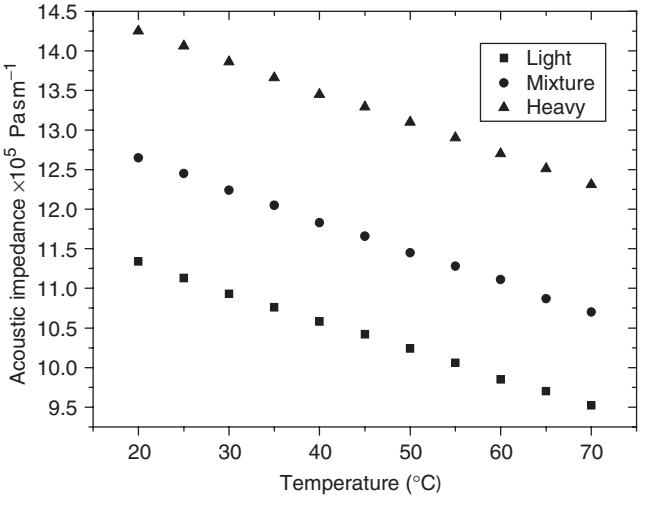

Figure 6. Acoustic impedance *vs.* temperature for light, heavy, and mixture of crude oils.

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$$Z(t) = [15.020 - 0.039(t - t_r)] \times 10^5 \quad \text{(Heavy)} \tag{12b}$$

$$Z(t) = [13.412 - 0.039(t - t_r)] \times 10^5 \quad \text{(Mixture)}. \tag{12c}$$

It has been observed that the heavy oil has larger acoustic impedance, almost 5% higher than that of the light oil. The acoustic impedance of the mixture falls between that of heavy and light oil.

The maximum transmission of a pressure wave across two adjoining liquids occurs when their impedances, Z_1 and Z_2 are equal. The pressure transmission coefficient (t_p) and the reflection coefficient (r_p) at the interface can be evaluated as,

$$t_p = \frac{2Z_2}{Z_1 + Z_2}, \tag{13}$$

$$r_p = \frac{Z_2 - Z_1}{Z_1 + Z_2}. \tag{14}$$

For a large acoustic impedance contrast ($Z_1 >> Z_2$), one gets $r_p \to -1$ and $t_p \to 0$, i.e. nearly all of the elastic wave is reflected. At such interfaces there is a phase change of 180° for the pressure. For $Z_1 \approx Z_2$, one has $r_p \to 0$ and $t_p \to 1$, as if there were one uniform medium and there is no reflection. The values of acoustic impedance should be of great significance to analyze the transmission and reflection of elastic waves at liquid interface. In particular, it becomes quite significant when elastic wave crosses the interface between the layers of hydrocarbon fluids and brines. Thus the above data is very useful in exploration geophysics where reflection and transmission of pressure (acoustic) waves are used for the discovery of oil trapped beneath the surface of the earth.

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4. Correlation between thermodynamic and thermo-elastic functions

The ideal $T\,\mathrm{d}s$ equation of thermodynamics is very useful to establish a link between the thermodynamic and thermo-elastic functions, i.e.,

$$T\mathrm{d}s = C_\Omega \mathrm{d}T + T\left(\frac{\partial P}{\partial T}\right)_V = C_P \mathrm{d}T - T\left(\frac{\partial \Omega}{\partial T}\right)_P \mathrm{d}P. \tag{15}$$

The last two identities of equation (15) readily yield:

$$C_P - C_\Omega = T\left(\frac{\partial \Omega}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_\Omega. \tag{16}$$

For a hydrostatic system, one also has

$$\left(\frac{\partial P}{\partial T}\right)_\Omega = -\left(\frac{\partial \Omega}{\partial T}\right)_P \left(\frac{\partial P}{\partial \Omega}\right)_T, \tag{17}$$

therefore equation (16) becomes

$$C_P - C_\Omega = -T\left(\frac{\partial \Omega}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial \Omega}\right)_T. \tag{18}$$

Since

$$\left(\frac{\partial\Omega}{\partial T}\right)_{\mathrm{P}} = \beta\Omega;\ \left(\frac{\partial\Omega}{\partial P}\right)_{\mathrm{T}} = -\kappa_T\Omega(\kappa_T = \text{isothermal compressibility}) \text{ and}$$
$$\frac{C_{\mathrm{P}}}{C_\Omega} = \frac{\kappa_T}{\kappa_S} = \gamma,$$

equation (18) leads to the value of the ratio of the specific heats (γ), i.e.,

$$\gamma = 1 + \frac{T\Omega\beta^2}{C_{\mathrm{P}}\kappa_{\mathrm{S}}}. \tag{19}$$

Equation (19) can be used to determine γ as all the functions of the right hand side have been obtained directly from experiments in earlier sections. The values of β and the adiabatic compressibility κ_{S} as a function of temperature was determined in earlier sections.

The values of γ for light, heavy, and mixture of crude oils are computed from equation (19). The computed values are found to be almost independent of temperature. Average value of γ for light crude oil is around 1.21, for heavy oil it is around 1.13, and for the mixture around 1.20. Though the mixture has a 50 : 50 composition, γ is not the average of light and heavy values. It can be noted that γ of the mixture is closer to the value of light oil. We may compare these values to the standard theoretical results from ideal gas model. γ varies from 1.33 for polyatomic system to 1.67 for monatomic system. Obviously our determined values of γ suggests complex molecular bonds in the whole range of temperatures of investigation.

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5. Isothermal compressibility and specific heat at constant volume

The available experimental data of C_{P} and κ_{s} along with our values of γ can readily be used to determine isothermal compressibility κ_{T} and the specific heat at constant volume,

$$\kappa_T = \gamma\kappa_S, \tag{20}$$

$$C_\Omega = \frac{C_{\mathrm{P}}}{\gamma}. \tag{21}$$

The computed values of (κ_{T}) as a function of temperature for light, heavy, and mixture crude oils are presented in figure 7. For the three samples, κ_{T} increases with the increasing temperature. The temperature gradient of κ_{T} for the three samples differs slightly from one another. κ_{T} for light oil exhibits higher temperature-dependence than the heavy and mixture of oils. For example, κ_{T} for light oil is about 47% higher than the value of heavy oil at 20°C.

The values of C_Ω obtained from C_{P} and γ are plotted in figure 8. C_Ω for most of the liquid metals at their melting temperatures are found to be quite closer to the Dulong and Petit value of 3R except few odd cases like Cs ($C_\Omega \approx 4.7$R) and Te ($C_\Omega \approx 4.4$R). Other liquid alkali metals (Na, K, and Rb) are also found to have C_Ω values higher than $3R$ at their melting temperatures. C_Ω decreases with increasing temperatures but the gradients vary significantly from one to another liquid metal. For Te and Se, it almost

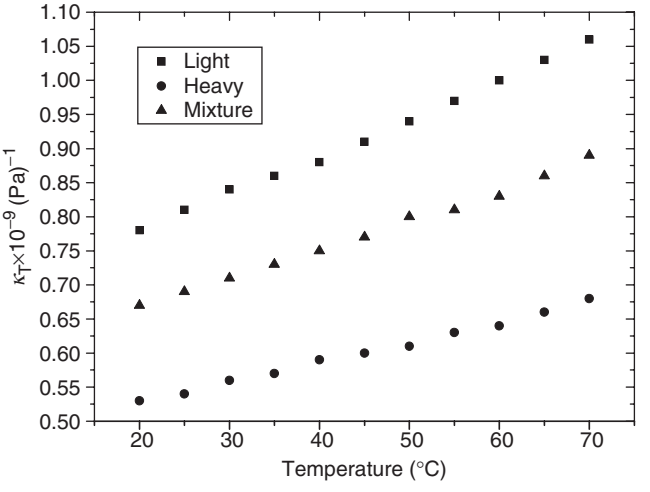

Figure 7. Variation of isothermal compressibility (κ_T) with temperature for light, heavy, and mixture of crude oil.

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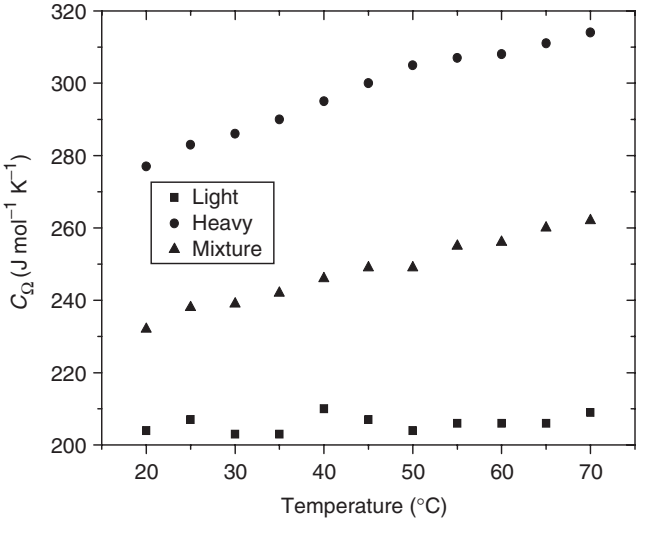

Figure 8. Variation of specific heat at constant volume (C_Ω) with temperature for light, heavy, and mixture of crude oil.

remains constant with increasing temperature. dC_Ω/dT for Fe is very small, whereas for *C*s it is very large. For other alkali metals the temperature gradient of C_Ω is also large.

6. Pressure–temperature dependence through ultrasonic measurements

The importance of the acoustic properties of reservoir liquid hydrocarbons is of many fold. The velocity of compressional wave and density of liquid hydrocarbon measured as a function of temperature offer a potentially favorable route for the *in-situ*

characterization of pressure–temperature dependence of reservoir liquids in a given well.

From the basic definition of the coefficient of volume expansion, $\beta\left[=\frac{1}{\Omega}\left(\frac{\mathrm{d}\Omega}{\mathrm{d}T}\right)_P\right]$ and the isothermal compressibility, $\kappa_T\left[=\frac{1}{\Omega}\left(\frac{\mathrm{d}\Omega}{\mathrm{d}T}\right)_T\right]$, one readily has

$$\mathrm{d}P = \frac{\beta}{\kappa_t}\mathrm{d}t. \tag{22}$$

For a change of finite temperature from a reference state t_r to a temperature t at a constant volume, the corresponding pressure changes from the reference pressure P_r to a pressure P. On integrating equation (22) from the reference state (P_r, t_r) to any other state (P, t), one gets,

$$P = P_\mathrm{r} + \int_{t_\mathrm{r}}^{t}\left(\frac{\beta}{\kappa T}\right)\mathrm{d}t. \tag{23}$$

We have used the temperature-dependence of the measured value of β and κ_T (given in figures 4 and 7) to determine β/kT as a function of t. It is found that β/kT for light, heavy, and the mixture of crude oils vary linearly with temperature,

$$\frac{\beta}{\kappa_T} = a - bt \tag{24}$$

where a and b are constants for light oil ($a = 1.1638 \times 10^6$, $b = -4.8456 \times 10^3$), heavy oil ($a = 1.3734 \times 10^6$, $b = -4.8495 \times 10^3$) and mixture of light and heavy oil ($a = 1.3595 \times 10^6$, $b = -5.1122 \times 10^3$). On substituting this in equation (23) we obtain the pressure and temperature dependence of light, heavy, and mixture of liquid hydrocarbons,

$$P = P_r + 1.1638 \times 10^6(t - t_r) - 2422.797(t^2 - t_\mathrm{r}^2) \quad \text{(Light)} \tag{25a}$$

$$P = P_r + 1.3734 \times 10^6(t - t_\mathrm{r}) - 2424.718(t^2 - t_\mathrm{r}^2) \quad \text{(Heavy)} \tag{25b}$$

$$P = P_r + 1.3495 \times 10^6(t - t_\mathrm{r}) - 2556.112(t^2 - t_\mathrm{r}^2) \quad \text{(Mixture)} \tag{25c}$$

P_r and T_r refer to the reference state. Equation (25) suggests that unlike many other thermo-elastic properties, the variation of P and t are no longer a linear behaviour. Further, the pressure–temperature behaviour of heavy oil and the mixture are close to each other and differ from the light oil.

7. Summary and conclusion

The physical and thermodynamic properties of light and heavy crude oil and their mixture were investigated. Density, velocity of compression wave (ultrasound), and the specific heat at constant pressure were measured directly from experiment for a range of temperature varying from 20 to 70°C. These data were, further, utilized to infer thermo-physical properties by utilizing thermodynamic relations.

Within the considered range of temperature, the ultrasound velocity (V) and the density (ρ) of the oil was found to decrease linearly with increasing temperature.

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Both V_{mix} and ρ_{mix} of the mixture are close to the ideal values of mixing. It has been observed that the velocity decreases linearly with increasing temperature. The temperature dependence of density and velocity were further used to determine the coefficient of volume expansion (β), adiabatic compressibility (κ_s) and the acoustic impedance (Z). β increases linearly with increasing temperature. β for light oil and mixture are very close to each other and larger in magnitude than the value for heavy oil. κ_s also increases with increasing temperature. κ_s for light oil is larger than the heavy oil. Acoustic impedance (Z), on the other hand, decreases with increasing temperature. The value of Z for mixture lies between the two values of light and heavy oils but exhibits a closer proximity to light oil. The specific heat at constant pressure (C_P) measured for light oil is found to be about 27% smaller than that of heavy oil near the room temperature. The value for the mixture is very close to the average value of light and heavy oils. The temperature-dependence of C_P of light oil is more interesting than other properties. We observed that the values of C_P for heavy oil and mixture of heavy and light oil increase linearly with increasing temperature but it remains almost independent of temperature for light oil.

The observed values of specific heat at constant pressure, coefficient of volume expansion, and the adiabatic compressibility are further used to determine the ratio of the specific heat (γ). We may emphasize that γ cannot be determined directly from the experiments; hence our approach is a potentially favorable route and *vis-à-vis* it does not involve any disposable parameter. γ for light oil and mixture are found to be very close to each other. For the heavy oil γ is about 7% more than that of the light oil. γ for all the samples are found to be independent of temperature.

From the known values of γ, the isothermal compressibility (κ_T) and the specific heat at constant volume (C_Ω) for the three samples were determined by utilizing thermodynamic equations. κ_T of light oil is about 47% higher than the heavy oil. The values of mixture are slightly higher than the average value. κ_T for all the samples increase with increasing temperature. Like C_P, C_Ω for heavy oil and the mixture increase with increasing temperature but both C_P and C_Ω for light oil remains invariant with temperature.

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