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THERMODYNAMIC CONSISTENCY BETWEEN CALORIMETRIC ACOUSTIC AND VOLUMETRIC MEASUREMENTS

Application to *n*-undecane

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In this work, experimental measurements of isobaric heat capacity as well as speed of sound were performed in the compressed liquid phase of *n*-undecane from 303.15 to 373.15 K and for pressures ranging up to 60 MPa. These results were used to estimate various thermophysical properties such as density, isentropic compressibility and isochoric heat capacity in the same ranges of pressure and temperature. All these sets of data allow checking the thermodynamic consistency between calorimetric, acoustic and volumetric properties.

Keywords: *heat capacity, isentropic and isothermal compressibilities, speed of sound, n-undecane*

Introduction

Second-order thermodynamic properties, such as compressibility, thermal expansion coefficients and heat capacity, play an important role in the oil and gas industry. The knowledge of the volumetric behaviour of reservoir fluids is essential during production and transport operations whereas heat capacity C_P is an essential property to perform thermal calculations in all heat transfer processes. Moreover amongst these second order properties heat capacities occupies a special place due to its relation with entropy, i.e. $C_p=T(\partial S/\partial T)_p$ which provide information on the microscopic structure of the system. As a result, the accurate measurement and comprehensive modeling of these second-order properties for liquids and their mixtures are of interest to both the improvement of our knowledge of liquid structure and to optimization of many processes in oil and gas engineering.

It is well known that most classical equations of state (EOS) present serious limitations for describing second-order properties the main reason for this being that they have been developed to describe phase equilibria [1, 2]. As long as the complexity of the system, as for instance the molecular chain increases which is the case of components which belong to the heavy fraction of the crude oil, additional shortcomings appear. In this context of special relevance is the work of Llovell *et al.* [3], Vijande *et al.* [4] and Lafitte *et al.* [5] which propose a complete thermodynamic description i.e. phase equilibria and thermodynamic behavior from a single approach using the same molecular EOS, namely the SAFT in different versions. In addition it has been demonstrated [5] the interest of adding thermodynamic properties namely densities and speed of sound to the classical fitting procedure based on the LV equilibrium. This procedure yields between accuracies of the estimated properties and at the same time, parameters with a stronger physical meaning. In view of the application of these models to complex multi-components systems like reservoir fluids, it is of primordial to have large database for pure system in hand to test and to develop, the models.

In this context, the main goal of this work is to provide reliable data of thermodynamic properties and their temperature and pressure dependence. To this end, attention was focused on the experimental determination of molar isobaric heat capacities $C_{p,m}(P,T)$ and speed of sound $c(P,T)$ for *n*-undecane, a normal alkane which belongs to the above mentioned heavy fraction. Then, using this set of data, density, isentropic and isothermal compressibility and isochoric heat capacity were determined in the same $[p,T]$ ranges. The consistency between calorimetric, acoustic and volumetric data is then checked [6].

Experimental

Materials

n-undecane was supplied from Fluka (purity, 99 mol%) and used without further purification.

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Methods

Acoustic measurements

The ultrasound velocity was measured by using a pulse echo transmission–reflection technique operating at 3 MHz. The apparatus, described previously in detail [7], is essentially made up of an autoclave cell closed at both ends by two identical plugs on which PZT piezoelectric elements are fixed. One acts as pulse transmitter/receiver whereas the second as a receiver only. The traveling time of the wave through the sample was determined from the measurement, by direct chronometry [8], of the first echo as well as the signal which has done a round trip in one of the plug by means of a numerical oscilloscope. The length of the sample path was determined precisely at each temperature and pressure condition by calibration with water [9, 10]. The uncertainty in the speed of sound determined from this procedure, was estimated taking into account the temperature and pressure effects on the path length to be about 0.2% over the entire P–T range. The high-pressure cell was immersed in a controlled and stirred liquid bath, which provides thermal stability of 0.02 K. Temperatures were measured using platinum probes (Pt100) embedded inside the cell and linked to high accuracy thermometer (AOIP brand). The uncertainty in the temperature measurements is estimated to be ±0.1 K. The pressure, generated by a high-pressure pneumatic pump was measured by a high-pressure transducer frequently checked against a dead mass tester to an accuracy of better than 0.02% full scale. This approach is of special interest when the apparent ultrasonic velocity u measured in fluids coincides with the speed of sound c within the low frequency boundary and if the fluid remains in single phase state. In these conditions, the speed of sound is a thermodynamic parameter linked to a reversible adiabatic process, and can be defined by the thermodynamic relationship:

$$c^2 = \frac{1}{\rho\kappa_s} \tag{1}$$

where κ_S is the isentropic compressibility and ρ is the density.

Heat capacity measurements

Heat capacities C_p were determined with a Setaram C80 calorimeter based on the Calvet principle and adapted as a pressure scanning calorimeter [11]. The scanning method was used; that is, a temperature variation at a constant rate (0.15 K min^{-1}) was induced under isobaric conditions and the calorimetric response was simultaneously recorded. Since this calorimetric signal is proportional to the volumetric heat capacity, the obtention of the molar heat capacities, C_p entails densities, ρ, data. In the case of *n*-undecane, recommended densities data were available in literature [12]. The estimated uncertainty on C_p, based mainly on the estimated errors due to the calibration constant, is inferior to 0.5%. Detailed information on both pressure implementation and calibration procedure can be found in references [13–15].

Results and discussion

Speed of sound measurements were carried along isotherms spaced at 10 K intervals from 303.15 to 373.15 K in the pressure range from atmospheric pressure to 60 MPa using 10 MPa steps. The speed of sound values obtained are given in Table 1 and plotted as a function of pressure in Fig. 1. The data were fitted to a rational function which correlates c^2 with nine adjustable parameters:

$$\{c/(\text{m s}^{-1})\}^2 = \frac{E+Fp/\text{MPa}}{A+Bp/\text{MPa}+C(p/\text{MPa})^2+\text{D}(p/\text{MPa})^3} \tag{2}$$

where:

$$A = A_0 + A_1 T/K + A_2 (T/K)^2 + A_3 (T/K)^3 \tag{3}$$

$$E = 1 + E_1 T/K \tag{4}$$

The parameters obtained by a least squares method are listed in Table 2 along with the average deviation (AD), the average absolute deviation (AAD)

Table 1 Experimental speed of sound values c (m s^{-1}) for *n*-undecane

P/MPa	Temperature/K							
	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
0.1	1240.5	1201.8	1163.2	1124.9	1087.4	1050.7	1015.2	980.8
10	1299.5	1263.9	1228.2	1193.0	1158.5	1124.9	1092.4	1061.2
20	1354.2	1320.9	1287.5	1254.6	1222.3	1191.0	1161.9	1132.0
30	1405.0	1373.5	1341.9	1310.8	1280.3	1250.7	1222.3	1195.3
40	1452.4	1422.4	1392.3	1362.6	1333.5	1305.3	1278.3	1252.7
50	1496.6	1467.8	1439.0	1410.4	1382.5	1355.5	1329.7	1305.2
60	1537.5	1509.8	1482.0	1454.5	1427.6	1401.6	1376.7	1353.3

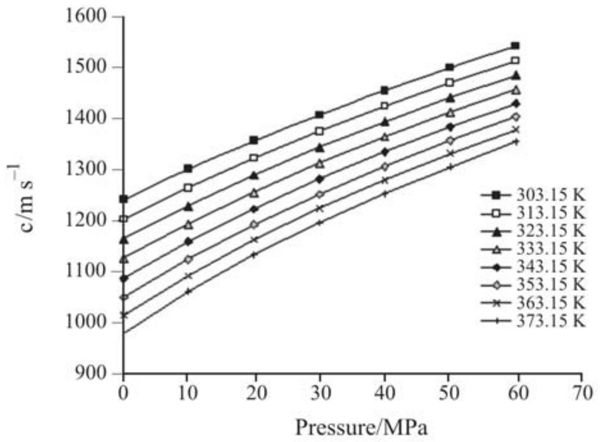

Fig. 1 Experimental speed of sound c (m s^{-1}) data as a function of pressure (isothermal curves) for *n*-undecane

Table 2 Parameters of Eqs (2) to (4)

Parameters	*n*-undecane
A_0/m^{-2} s^2	$1.27913\cdot10^{-6}$
A_1/m^{-2} s^2 K^{-1}	$-1.03210\cdot10^{-8}$
A_2/m^{-2} s^2 K^{-2}	$3.37846\cdot10^{-11}$
A_3/m^{-2} s^2 K^{-3}	$-3.42830\cdot10^{-14}$
B/m^{-2} s^2 MPa^{-1}	$2.42278\cdot10^{-9}$
C/m^{-2} s^2 MPa^{-2}	$-1.52270\cdot10^{-11}$
D/m^{-2} s^2 MPa^{-3}	$8.10545\cdot10^{-14}$
E_1/K^{-1}	$-1.7773\cdot10^{-3}$
F/MPa^{-1}	$8.39105\cdot10^{-3}$
AD%	$-2.7\cdot10^{-4}$
AAD%	$3.4\cdot10^{-2}$
MD%	$1.7\cdot10^{-1}$

and the maximum deviation (MD). These deviations which are less than the experimental error show that the function leads to a good interpolation of the speed of sound data. A comparison lead at the atmospheric pressure with data found in the literature [6–8] reveals a good agreement with an absolute average deviation inferior to 0.1%.

Molar heat capacities were determined from 313.15 to 373.15 K at different pressure ranging from the atmospheric to 60 MPa. They were fitted to a polynomial form [16] at each pressure:

$$C_p = \sum_{i=0}^{n} B_i \left(\frac{T}{100}\right)^i \qquad (5)$$

The values of the coefficients B_i together with the absolute average deviation AAD (%) are listed in Table 3. Comparisons with data available in literature at the atmospheric [16] and under pressure [17] show deviations always inferior to 0,1%. Molar isobaric heat capacities are plotted as a function of temperature in Fig. 2.

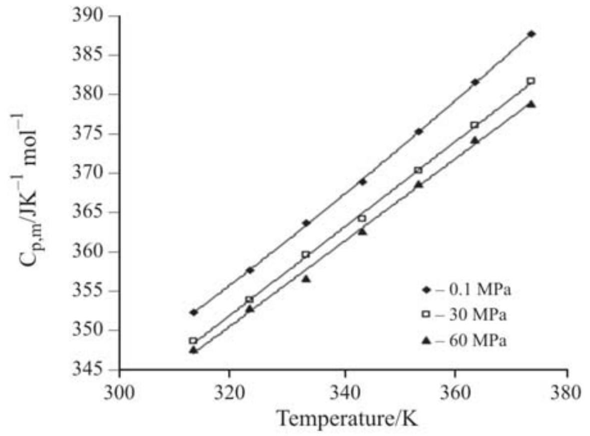

Fig. 2 Experimental molar isobaric heat capacities $C_{p,m}$ (J K^{-1} mol^{-1}) as a function of temperature for *n*-undecane

Thermodynamic consistency

The isentropic compressibility κ_S is related to the isothermal compressibility κ_T by the following expression:

$$\kappa_T - \kappa_s = T\alpha_p^2/(\rho C_p) \qquad (6)$$

where α_p corresponds to the isobaric thermal expansion coefficient. This expression is a key relation which involves volumetric, calorimetric and acoustic (or adiabatic) properties. Of special relevance is the fact that the compressibility tends to a limit value in the condensed liquid state which is traduced by a very small contribution of the term on the right-hand side of Eq. (6). Thus a goal of the present work is to use speed of sound and heat capacity measurements together with literature density data in order to the check if anyone of them can be estimated from knowing the others properties by use of Eq. (6).

For instance, a first approach consists in expressing density from speed of sound and heat capacity by use of an integrated form with respect to pressure of Eq. (6):

$$\begin{aligned}&\rho(p,T) - \rho(p_0,T) = \\ &= \int_{p_0}^{p} 1/c^2 \mathrm{d}p + T\int_{p_0}^{p} (\alpha_p^2/C_p)\mathrm{d}p\end{aligned} \qquad (7)$$

where p_0 is a reference pressure equal to 0.1013 MPa in this case. This expression allows calculating high-pressure densities from ultrasonic measurements for a fluid provided that density and heat capacity at the reference pressure are known in order to initiate the integration procedure. Thus, the atmospheric values of C_p result from the literature [16] as well as the atmospheric density data [12]. The first term on the right-hand side of Eq. (3), is evaluated by analytical integration of Eq. (2). The last term, which can be assimilated to an adiabatic perturbation of the

Table 3 Coeffcients B_i of Eq. (5) and absolute average deviations AAD (%) of fit for molar heat capacities $C_p(P, T)$ of *n*-undecane

P/MPa	Parameters				
	A_1	A_2	A_3	A_4	AAD (%)
0.1	40.886	–7.4886	3.198	–0.2089	0.031
10	0.4677	29.084	–7.8079	0.8878	0.030
20	–43.616	67.934	–19.163	1.9845	0.030
30	36.477	–4.1339	2.3694	–0.1567	0.030
40	135.12	–93.069	29.043	–2.8201	0.028
50	216.3	–163.29	49.237	–4.7524	0.030
60	329.8	–260.97	77.198	–7.4159	0.030

Table 4 Estimated isentropic compressibilities κ_s (GPa^{-1}) for *n*-undecane

P/MPa	Temperature/K							
	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
0.1	0.887	0.954	1.029	1.112	1.203	1.303	1.411	1.529
10	0.800	0.854	0.913	0.977	1.046	1.120	1.200	1.285
20	0.730	0.774	0.822	0.874	0.929	0.987	1.049	1.113
30	0.673	0.710	0.750	0.792	0.838	0.885	0.935	0.986
40	0.624	0.656	0.691	0.727	0.765	0.805	0.846	0.888
50	0.584	0.612	0.641	0.673	0.706	0.740	0.775	0.810
60	0.550	0.574	0.600	0.628	0.657	0.686	0.716	0.747

Table 5 Estimated isothermal compressibilities κ_T (GPa^{-1}) for *n*-undecane

P/MPa	Temperature/K							
	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
0.1	1.074	1.153	1.241	1.337	1.442	1.557	1.682	1.818
10	0.963	1.024	1.092	1.165	1.244	1.328	1.419	1.515
20	0.874	0.924	0.977	1.035	1.097	1.163	1.232	1.305
30	0.802	0.843	0.887	0.934	0.984	1.037	1.093	1.150
40	0.742	0.777	0.814	0.853	0.895	0.939	0.985	1.032
50	0.692	0.722	0.753	0.787	0.822	0.860	0.898	0.938
60	0.650	0.675	0.703	0.732	0.763	0.795	0.828	0.862

second one, is computed iteratively using a predictor–corrector procedure already presented in a previous paper [18]. The isobaric expansion coefficient, present in this latter integral, is determined at each pressure step by differentiation of density with respect to temperature, whereas the heat capacity is found at each stage of the calculation from:

$$C_p(p,T)-C_p(p_0,T)= =-\int_{p_0}^{p}\frac{T[\alpha_p^2+(\partial\alpha_p/\partial T)_p]}{\rho}\mathrm{d}P \tag{8}$$

The comparisons between the estimated values and the experimental one show absolute average deviation AAD (%) of 0.12 and 0.1% for density and heat capacity respectively. No data were available for the isobaric thermal expansion coefficient. This approach largely used for density seems adapted enough to provide reliable estimations of heat capacity. Isentropic and isothermal compressibilities using Eqs (1), (6) and (7) are reported in Tables 4 and 5, respectively.

The thermodynamic consistency could be also used in an other way. Indeed, from the simultaneous knowledge of heat capacity $C_{p,m}(p,T)$ and density $\rho(p,T)$ one can calculate speed of sound with a very good accuracy [19]. Recommended density data available in literature [12] were used and fitted to a modified Tait equation [20] to calculate the isothermal compresibility coefficient κ_T. As already mentioned [20], it is more advisable to estimate the isobaric thermal expansivity from a numerical derivation of density data. Then, isentropic compressibility and ultrasound velocity can be deduced from relations (1) and (6) respectively. A comparison lead between experimental and estimated speed of sound data shows AAD (%) around 1% between the two sets of data which ratifies the consistency of this methodology. Finally, molar isochoric heat capacities $C_{V,m}$ were calculated by using the following exact thermodynamic relation:

$$C_V = C_p - T\alpha_p^2/(\rho\kappa_T) \qquad (9)$$

Figure 3 illustrates the temperature dependence for $C_{V,m}$ (molar isochoric heat capacity) in the case of several isobaric curves. Finally it is worth recalling that in the framework of Nan [21] thermodynamic functions could be easily derived from the knowledge of heat capcities which provide useful information for some systems.

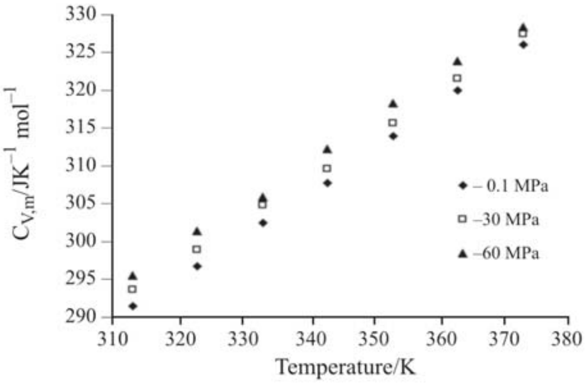

Fig. 3 Estimated molar isochoric heat capacities $C_{V,m}$ (J K^{-1} mol^{-1}) as a function of temperature for *n*-undecane

Conclusions

A methodology based on the thermodynamic consistency between accoustic, volumetric and calorimetric properties in the compressed liquid state is proposed to obtain a whole thermophysical characterization in large pressure and temperature ranges. Thus, a complete thermophysical characterization is proposed for *n*-undecane. In addition the interest of combining different properties to obtain a complete charcaterisation has been demonstrated. The approach presented here could be easily extended to complex multi-components mixtures like reservoir fluids without further complication.

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