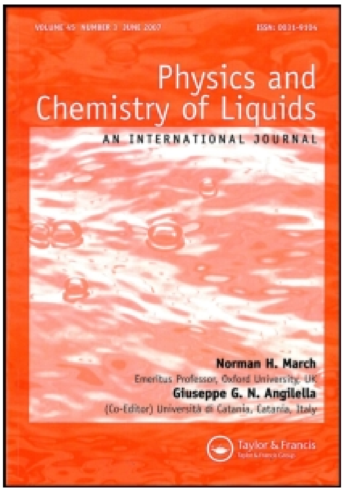

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ACOUSTIC DETERMINATION OF THERMODYNAMIC PROPERTIES OF TERNARY LIQUID MIXTURES UP TO 150 MPA

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Ultrasonic velocity measurements were carried out on two ternary mixtures at pressures up to 150 MPa and within a temperature interval of 293 K – 373 K. The first of these two mixtures, which was selected to simulate a distillation cut close to 423 K, is made up (in mass percentage) of 40% nonane, 35% cyclooctane and 25% propylbenzene; the second, made up of 40% undecane, 35% pentylcyclohexane and 25% pentylbenzene has a boiling point of approximately 473 K. The acoustic measurements were then used to characterize the pρT behaviour of these two ternary mixtures in the liquid state. They also provided indirect access to the isentropic and isothermal compressibility coefficients of these mixtures.

Keywords: Ternary mixtures; ultrasonic velocities

1. INTRODUCTION

It is well-known that crude oil from petroleum reservoirs is formed of a substantial number of hydrocarbon compounds belonging to various classes of compounds, the three most common of which are paraffins, aromatics and naphthenes. These components range from the lightest (which are gases in normal conditions), such as methane, ethane to extremely heavy components such as asphaltenes or bituminous residues. The composition is so complex that it is impossible to

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*Corresponding author.

identify rigorously the nature and proportion of each of the heavy components, and so it is common practice, when representing a real fluid to group together all elements including 11 or more carbon atoms within a single cut (known as the heavy C_{11+} cut).

So in order to simulate the thermodynamic behaviour of a crude oil, it is essential to be able to attribute acceptable values for the heavy cut, even though its composition is not defined in detail. Different hypotheses have been put forward to do this, and each oil-producing company has made its own choice among them. For example, some of them consider that the heavy fraction of a fluid can be considered as a single molecule with a molecular weight equal to that of the fraction, and this molecule is assumed to be composed of aliphatic, naphthenic and aromatic types in proportions identical to those of the same arrangements within the intermediary C_6-C_{10} fraction of the fluid. Thus, by continuity, the heavy C_{11+} cut reflects the same functional picture as the lighter C_6-C_{10} cut immediately below it.

According to the geographical origin of natural fluids, the molar proportion of the heavy fraction can vary by no more than a few %, in so-called light oils, to as much as some 40% in heavy oils. It is clear that in the latter case, prediction of the behaviour of the fluid as a whole will be strongly influenced by prediction of the behaviour of the heavy fraction. It is consequently important to be able to estimate the properties of the heavy fraction, with as little inaccuracy as possible, despite the highly hypothetical nature of data on its composition. In order to identify as clearly as possible the precise contribution it makes to the behaviour of a given real fluid, one needs to have experimental data over a range of temperatures and pressures concerning hydrocarbons containing large numbers of carbon atoms or mixtures of such substances, and with this aim in mind the most valuable properties are volumetric properties, phase equilibria and calorimetric properties. The speed of sound can also be a useful property, in so far as it is a thermodynamic property and can be used to calculate the various thermo-elastic coefficients.

We thus undertook an experimental and numerical investigation of ternary mixtures (involving the 3 chemical families mentioned above) in which the three components have practically identical boiling points. These mixtures, in which the molar content of each family is consistent with the average observations made on the overall composition of a number of crude oils, thus represent petroleum distillation cuts in simplified form. This paper looks at 2 distinct systems, in the first of which all the components belong to the heavy fraction (with the number of carbon atoms ≥ 11 and boiling point approximately 473 K) whereas the second cut is located at the boundary between the heavy and intermediate fractions with boiling points of the order of 423 K (and 8 to 9 carbon atoms). As well as these ternary systems, a pure substance (in this case normal heptane) was subjected to experimental study concerning ultrasonic velocity. This complementary study was done to test the reliability of our measurements compared with data in the literature. This is essentially due to the fact that the measurement cell used in the investigation is a new design and it seemed essential to compare the ultrasonic speed values obtained with those already published by other authors on a widely studied substance. The data referred to in this paper cover a very large pressure domain (0 – 150 Mpa) in temperature range from 293 to 373 K and reflect measurements of several thermodynamic properties: ultrasound velocity, density, and adiabatic and isothermal compressibilities.

This investigation follows a long series of activities undertaken by our laboratory into thermophysical characterization at high pressures of synthetic or natural mixtures of hydrocarbons in the liquid [1 – 3], or gaseous state [4 – 6].

2. EXPERIMENTAL TECHNIQUE

The experimental investigations on both ternary mixtures concerned ultrasonic velocity over the entire pressure and temperature intervals given above, as well as density over the entire temperature domain but at one fixed pressure (atmospheric pressure). On the basis of all these measurements and by means of an effective numerical procedure whose main stages will be presented below, we deduced the behaviour of density and of the isothermal and isentropic compressibility coefficients over the whole range of P and T intervals.

2.1. Ultrasonic Speed

The apparatus used to measure the speed of propagation of ultrasound waves (frequency 3 MHz) involves a number of different elements including:

- a signal transmission and reception system made up of an electrical impulse generator (PANAMETRICS 5055 PRM) and a numerical oscilloscope with memory storage (GOULD 4090)
- a measurement cell containing the fluid sample, of dimensions enabling it to withstand pressures higher than 200 MPa
- a two-chamber volumetric pump whereby pressure can be transmitted by means of compression oil (maximum operating pressure of the pump is of the order of 50 MPa)
- a pressure multiplier, with a characteristic ratio of 4.5, which in combination with the pump can generate pressures throughout the interval from atmospheric pressure to more than 200 MPa
- a mobile internal piston separator which places the required pressure on the fluid sample by means of the compression oil, without contact between the two fluids
- a heat-regulation system
- a set of pressure and temperature sensors.

More detailed information on these various parts of the apparatus can be found in the article by Daridon [7]. Only the measurement cell is different from the experimental set-up described previously; it is more compact than the previous one, its geometrical characteristics having been defined after deformation simulation tests. It is moreover made of a material which is particularly resistant to mechanical constraints and chemical corrosion and can thus withstand pressures above 200 MPa without damage.

The cylindrical cell, which is represented in diagram form in Figure 1, is closed at each end by two identical bars which function as a transmission medium between the piezo-electric transducers (fixed to the outsides of the bars) and the fluid sample. While the presence of bars facilitates transmission of the acoustic waves to the fluid, and at the same time protects the transducers from the pressure constraints imposed on the cell, it does however lead to successive reflections at the interfaces which complicate exploitation of the signals transmitted.

The result is that in some cases (for highly absorbent fluids like gases for example) only the first echo transmitted, associated with a direct trajectory, can be exploited. This explains why we abandoned the echo overlap method to determine transit time t_S of ultrasound waves within the sample. The procedure selected, developed by Daridon [7], is based on double measurement by direct chronometry of transit times by transmission and by reflection. Independently of the method used to measure t_S, determination of ultrasonic velocity (given by $u = L(P, T) \backslash t_S$) requires the length of passage L within the cell to be corrected for the effects of temperature and pressure. The expression adopted for $L(P, T)$, i.e.:

$$L(P,T) = L_0[1 + a(T - T_0)] \cdot [1 + b(P - P_0)] \tag{1}$$

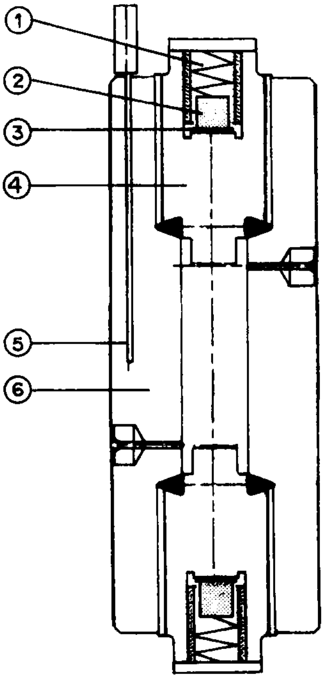

FIGURE 1 Ultrasonic measurement cell. (1): Spring, (2): Backing element, (3): Piezoelectric element, (4): Buffer, (5): Temperature probe, (6): Autoclave cylinder.

involves coefficients *a* and *b* dependent on the mechanical properties of the materials used in the autoclave cell. They were determined indirectly after measurement of the travel times of acoustic waves within the cell, first in the presence of water and then of pentane at different pressures and temperatures.

Parameters *a* and *b* were adjusted so as to reproduce the sound speed data [8–10] with an absolute average deviation less than 0.01%. After this preliminary calibration a series of ultrasonic velocity measurements were performed on normal heptane (FLUKA brand, purity > 99.5%) between 1 and 150 MPa and between 293.15 K and 373.15 K in order to verify the validity of our results by comparison with those in the literature. Table I and Figure 2 present all the ultrasonic velocity values which we measured for this pure substance using the above apparatus. As there is substantially more data in the literature for ultrasonic velocity in heptane at atmospheric pressure than at other pressures, the first comparison was restricted to values obtained at atmospheric pressure. All the data at $P = 1$ atm. (summarized in Tab. II) were first adjusted using a third degree polynomial taking account in the minimisation function of the experimental error announced by the authors. In the second stage the data in the base which proved inconsistent, i.e. which deviated by

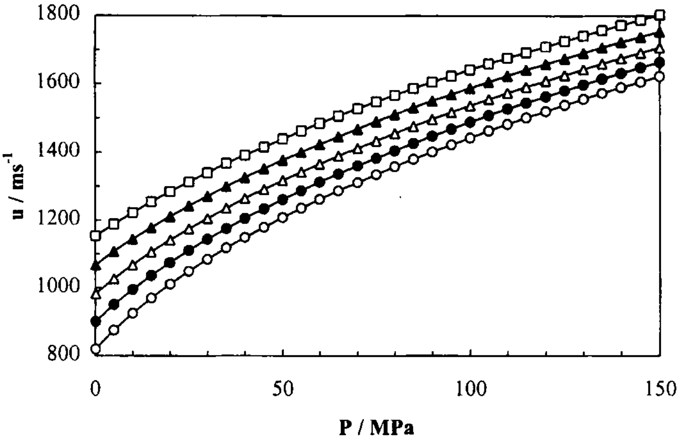

FIGURE 2 Speed of sound *u* in *n*-heptane as a function of pressure. -□-: 293.15 K; -▲-: 313.15 K; -△-: 333.15 K; -●-: 353.15 K; -○-: 373.15 K.

TABLE I Speed of sound u (ms^{-1}) measured in n-heptane as function of pressure and temperature

	T/K								
P/ Mpa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
0.1	1152.7	1109.9	1067.4	1024.7	982.4	941.7	900.6	859.7	819.0
5	1187.9	1147.2	1106.9	1066.1	1026.6	988.1	949.9	911.9	874.7
10	1221.9	1182.5	1144.0	1105.1	1067.6	1031.1	994.7	959.3	924.5
15	1253.8	1216.1	1178.4	1141.6	1105.5	1070.8	1036.0	1002.4	969.4
20	1284.2	1247.3	1210.7	1175.5	1140.5	1107.3	1074.2	1042.1	1010.4
25	1312.8	1277.2	1242.1	1207.5	1174.0	1141.4	1109.7	1078.8	1048.5
30	1340.2	1305.7	1271.3	1238.0	1205.2	1174.1	1143.2	1113.2	1083.9
35	1367.2	1332.5	1299.4	1267.0	1235.4	1204.8	1174.7	1145.9	1117.4
40	1392.1	1359.1	1326.4	1294.6	1263.7	1234.1	1204.7	1176.7	1148.9
45	1416.2	1383.9	1352.5	1321.3	1290.9	1261.9	1233.4	1206.0	1179.1
50	1439.9	1408.2	1377.3	1346.8	1316.8	1288.6	1260.8	1234.2	1207.6
55	1463.1	1431.6	1401.2	1371.4	1341.9	1314.3	1287.1	1260.8	1235.3
60	1484.8	1454.5	1424.5	1395.2	1366.5	1339.1	1312.5	1286.7	1261.7
65	1506.2	1476.3	1447.0	1417.9	1389.9	1362.9	1337.0	1311.7	1286.9
70	1527.1	1497.6	1468.7	1440.1	1412.8	1386.1	1360.9	1335.7	1311.4
75	1547.4	1518.2	1489.8	1461.7	1434.7	1408.6	1383.4	1359.3	1335.0
80	1566.8	1538.4	1510.4	1482.8	1456.2	1430.6	1405.7	1381.3	1358.0
85	1586.2	1557.6	1530.4	1503.0	1476.4	1451.7	1426.9	1403.3	1380.0
90	1605.1	1577.1	1550.1	1523.0	1496.8	1472.4	1448.1	1424.6	1401.7
95	1623.2	1595.9	1569.0	1542.5	1516.6	1492.5	1468.5	1445.2	1422.6
100	1641.5	1614.1	1587.4	1561.2	1535.9	1511.9	1488.1	1465.1	1443.1
105	1659.0	1632.0	1605.6	1579.7	1554.7	1530.9	1507.7	1485.0	1462.9
110	1676.2	1649.5	1623.5	1598.2	1573.0	1549.7	1526.4	1504.2	1482.4
115	1692.8	1666.8	1641.2	1615.7	1591.1	1567.8	1544.6	1522.7	1501.3
120	1709.4	1683.7	1658.2	1633.1	1608.9	1585.9	1562.9	1541.1	1519.7
125	1725.8	1700.1	1674.9	1650.0	1625.9	1603.4	1580.6	1559.0	1537.9
130	1741.8	1716.4	1691.5	1666.9	1642.9	1620.5	1598.1	1576.7	1555.7
135	1757.5	1731.9	1707.4	1683.0	1659.5	1637.0	1615.1	1593.6	1573.2
140	1772.7	1747.7	1723.2	1698.9	1675.6	1653.4	1631.9	1610.5	1590.2
145	1788.4	1763.2	1738.6	1714.8	1691.8	1669.8	1648.4	1627.0	1606.8
150	1803.2	1777.7	1754.1	1730.3	1707.5	1685.7	1664.3	1643.4	1623.2

TABLE II References of sound speed data u measured in n-heptane at atmospheric pressure

authors	*Tmin – Tmax*	*Nb Points*	*References*
Aminabhavi *et al.*	298.15	1	11
Boelhouwer	253.15 – 353.15	6	12
Freyer *et al.*	273.15 – 323.15	6	13
Geelen *et al.*	298.15	2	14
Junquera *et al.*	298.15	1	15
Kumaran *et al.*	298.15	1	16
Muringer *et al.*	185.65 –298.15	9	17
Schaafs	298.15	1	18
Sachdeva	293.15 –353.15	8	19
Tamura *et al.*	298.15	1	20
Tardajos *et al.*	298.15	1	21
Wang *et al.*	265.15 –368.15	15	22
Wilson *et al.*	298.15 –323.15	3	23

more than 0.5% from the predictions of the smoothing function, were withdrawn from the reference set. The parameters of the polynomial were then readjusted for this reduced base, with increased weight allocated to measurements at 298 K, as they had proved the most consistent from one author to another.

The smoothing polynomial established in these conditions is written:

$$u = 3.2412.10^3 - 1.160971.10^1 T + 2.11193.10^{-2} T^2 - 1.9868.10^{-3} T^3 \tag{2}$$

Our own ultrasonic velocity values in heptane, deliberately kept out of the adjustment procedure, present an absolute average deviation (AAD%) of 0.05 and a maximum deviation of 0.1% with respect to the values generated by the polynomial as can be observed in Figure 3. It should be pointed out at this stage that the data in the literature show deviation between them of more than 1%, which justifies elimination of the inconsistent points.

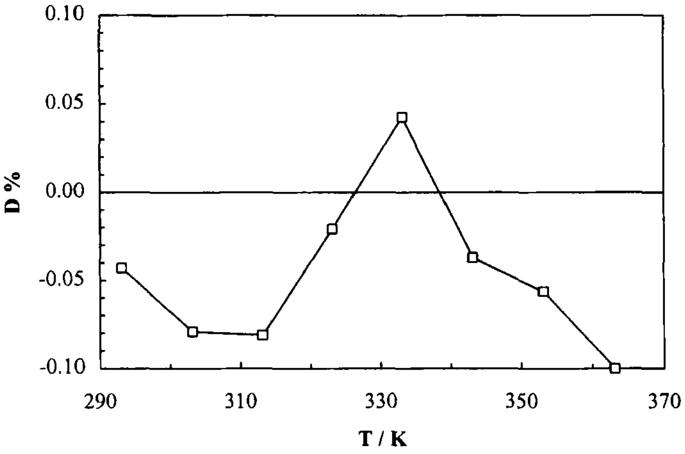

FIGURE 3 Deviations of sound speed u measured in n-heptane at atmospheric pressure with literature data smoothed by Equation 2.

A second comparison was carried out with reference to the data in the literature [12, 17] associated with pressures higher than atmospheric pressure. The test domain with respect to Boelhouwer's measurements [12] extends from 293 to 373 K and from 0.1 to 140 MPa. An AAD (%) of 0.045 and an AD (%) of 0.074 were observed between our measurements and those of Boelhouwer. As regards the measurements obtained by Muringer *et al.* [17], for which the test domain goes from 293 to 303 K and from 0.1 to 150 MPa, the respective values of the AAD (%) and AD (%) are 0.09 and 0.04 with values resulting from polynomial interpolation of our measurements. This interpolation was necessary because the measurement steps of pressure and temperature were not identical for the two data sets. These two comparisons reveal a very satisfactory fit between all the data at varying pressures: the deviations observed were of the same order of magnitude or even better than those observed at atmospheric pressure between the consistent data. These different tests enable us to conclude that the accuracy of our determinations of ultrasonic velocity is better than 0.1%.

2.2. Densities

The two ternary systems were subjected to complementary measurements of density, at atmospheric pressure, using an ANTON PAAR densitometer (DMA 60 model) in the temperature interval 293.15 K – 373.15 K (in 10 K steps). The operating principle of this experimental apparatus is to record the periods of oscillation of a *U*-shaped tube and to deduce its density which is related to the square of the period by a linear law whose two constants are determined by the method of Lagourette *et al.* [24]. The accuracy obtained by this experimental apparatus can be estimated at 0.05 kg/m^3 on the basis of the numerous comparisons carried out with reference to the work of other authors. Temperature within the apparatus is measured using a platinum probe linked to an AOIP brand calibrating thermometer.

3. EXPERIMENTAL RESULTS AND RELATED PROPERTIES CALCULATION

As we mentioned in our introduction, the two ternary mixtures include proportions by weight of 40% alkane, 35% naphthene and 25% aromatics; in each of these 2 mixtures, the representatives of the three families were selected as a function of their boiling points so that each mixture represents a distillation cut.

Thus the first system, S1, of molecular weight 120.62 g mole^{-1} is made up of components with boiling points of the order of 423 K whereas the components of the second system S2, whose molecular weight is 153.59 g mole^{-1} have boiling points close to 473 K. Table III presents the compositional characteristics of each of them. The paraffinic and aromatic compounds used in the preparation of the samples were FLUKA or ALDRICH brand and their degree of purity is better than 99%. The naphthenic compounds, supplied by the KASEI company, have a degree of purity higher than 98%.

As regards the ultrasonic measurements, nine isothermal curves in 10 K steps were plotted between 293 and 373 K, whereas the step adopted for pressure was 5 MPa. The two mixtures concerned are in the single-phase liquid state at atmospheric pressure, and so the pressure domain investigated runs from 0.1 MPa to 150 MPa. The isothermal and isobaric behaviour of ultrasonic velocity is displayed on Figures 4 and 5 respectively, and the corresponding values are presented in Table IV and Table V. We thus have almost 300 ultrasonic velocity data for each ternary mixture.

The propagation of acoustic waves within a fluid has the specific feature of being an adiabatic process and so on the basis of ultrasonic

TABLE III Mixtures properties

Systems	*Components*	*Formula*	T_b^*	*mass%*	*mole%*
	Nonane	C_9H_{20}	423.8 K	39.98%	37.47%
S1	Cyclooctane	C_8H_{16}	424.3 K	35.04%	37.54%
	Propyl-benzene	C_9H_{12}	430.2 K	24.98%	24.99%
	Undecane	$C_{11}H_{24}$	468.7 K	40.00%	39.29%
S2	Pentyl-cyclohexane	$C_{11}H_{22}$	476.9 K	35.00%	34.82%
	Pentylbenzene	$C_{11}H_{16}$	478.6 K	25.00%	25.89%

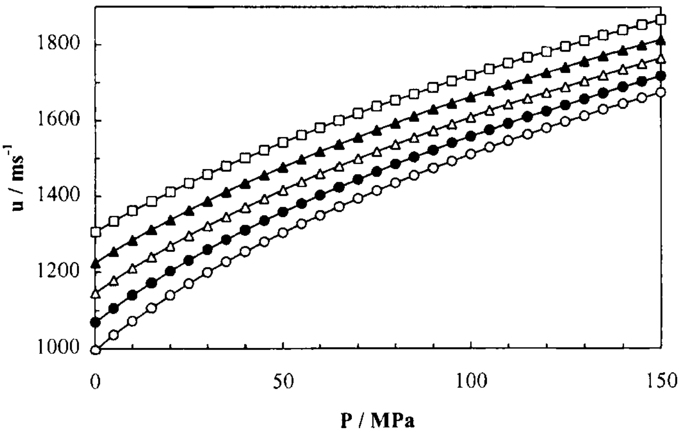

FIGURE 4 Speed of sound *u* in S1 as a function of pressure. -□-: 293.15 K; -▲-: 313.15 K; -△-: 333.15 K; -●-: 353.15 K -○-: 373.15 K.

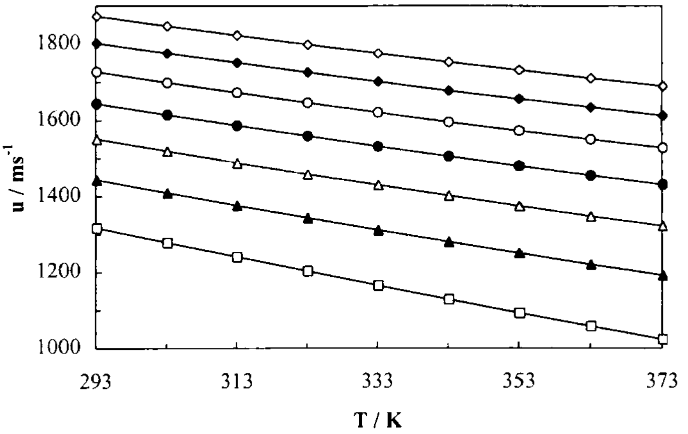

FIGURE 5 Speed of sound *u* in S2 as a function of temperature. -□-: 0.1 MPa; -▲-: 25 MPa; -△-: 50 MPa; -●-: 75 MPa; -○-: 100 MPa; -◆-: 125 MPa; -◇-: 150 MPa.

velocity measurements it is possible to obtain precise and direct information on the adiabatic properties of the fluid. However, in the case in which the experimental waves used belong to the ultrasound domain, assimilation of the velocity measured with the speed of sound assumes that there are no dispersive phenomena at frequencies lower

TABLE IV Speed of sound u (ms^{-1}) measured in S1 at temperature T and Pressure P

	T/K								
P/Mpa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
0.1	1305.6	1265.1	1224.5	1184.3	1145.4	1107.3	1069.2	1031.8	995.5
5	1333.9	1294.3	1255.0	1216.7	1178.9	1142.5	1105.5	1069.9	1035.7
10	1361.7	1322.2	1283.9	1246.7	1210.6	1174.1	1139.9	1105.3	1072.2
15	1386.2	1349.2	1311.7	1275.5	1240.2	1205.6	1171.8	1138.8	1106.1
20	1411.0	1374.4	1337.5	1303.0	1268.7	1235.2	1202.3	1170.2	1139.0
25	1434.7	1399.1	1363.1	1329.3	1295.9	1263.3	1231.1	1200.0	1169.8
30	1457.7	1422.7	1387.6	1354.1	1321.4	1289.8	1258.8	1228.2	1199.1
35	1479.9	1445.1	1411.7	1378.3	1345.7	1315.6	1285.1	1255.4	1226.8
40	1501.1	1467.5	1434.1	1401.5	1370.4	1339.7	1310.5	1281.2	1253.3
45	1522.2	1488.7	1455.7	1424.5	1393.3	1363.7	1335.2	1305.9	1278.8
50	1542.7	1509.8	1477.2	1446.5	1416.2	1387.0	1357.7	1329.7	1303.1
55	1562.2	1530.0	1498.0	1467.7	1438.3	1408.7	1380.3	1353.4	1327.0
60	1581.6	1549.4	1518.2	1488.3	1459.2	1430.2	1402.7	1375.4	1349.1
65	1600.4	1568.4	1537.7	1508.1	1479.5	1450.9	1423.7	1398.0	1372.0
70	1619.1	1587.1	1556.9	1527.4	1499.5	1471.5	1444.4	1418.8	1393.7
75	1638.1	1605.7	1575.7	1546.6	1518.6	1491.1	1465.0	1439.5	1414.4
80	1653.9	1623.2	1594.0	1565.1	1537.2	1510.5	1484.6	1459.2	1434.6
85	1670.8	1641.1	1612.1	1583.6	1555.8	1528.9	1503.4	1478.6	1454.4
90	1687.6	1657.7	1630.5	1601.4	1574.1	1547.9	1522.2	1497.5	1474.1
95	1704.7	1674.8	1646.5	1619.2	1591.8	1565.8	1541.2	1516.0	1492.5
100	1720.2	1690.6	1662.8	1635.0	1609.4	1583.2	1558.4	1534.3	1511.1
105	1735.8	1707.9	1678.8	1652.2	1627.6	1600.2	1575.8	1552.0	1529.7
110	1751.4	1722.6	1695.5	1668.3	1643.3	1617.0	1593.0	1569.3	1547.0
115	1766.9	1738.0	1711.2	1684.5	1659.0	1633.3	1610.3	1586.4	1564.1
120	1782.1	1752.4	1726.4	1700.5	1674.6	1649.9	1625.4	1602.8	1580.8
125	1796.3	1769.1	1741.9	1715.6	1690.3	1665.7	1641.7	1619.0	1597.8
130	1811.3	1783.4	1757.2	1730.8	1705.4	1681.5	1657.9	1635.3	1613.1
135	1825.5	1798.2	1771.3	1745.4	1721.0	1697.5	1673.6	1651.0	1630.3
140	1839.1	1812.4	1786.0	1760.3	1735.7	1712.0	1689.7	1666.6	1645.1
145	1853.3	1826.6	1800.6	1774.7	1750.8	1727.0	1704.3	1681.4	1660.3
150	1866.6	1840.3	1814.2	1788.8	1765.1	1741.4	1718.6	1695.9	1675.3

than that of the waves. This condition is generally satisfied by hydrocarbons at frequencies lower than a few tens of Mega Hertz, and thus by the systems considered in this work. So, the ultrasonic velocity u (which is identical with the speed of sound within the limit of zero frequencies C_0) corresponds to:

$$u^2 = \frac{1}{\rho k_S} \tag{3}$$

and can be linked with various thermophysical properties through the fluid's compressibility coefficient k_S. Because of the relationship

TABLE V Speed of sound u (ms^{-1}) measured in S2 at temperature T and Pressure P

	T/K								
P/Mpa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
0.1	1316.7	1277.7	1240.2	1202.3	1164.7	1128.1	1092.2	1057.1	1022.4
5	1343.9	1306.2	1269.4	1232.7	1196.6	1161.4	1127.2	1093.5	1060.5
10	1370.7	1333.9	1297.7	1262.4	1227.8	1193.5	1160.3	1127.7	1096.0
15	1395.9	1359.7	1325.4	1290.6	1256.6	1223.7	1191.6	1160.2	1129.6
20	1420.3	1385.4	1351.4	1317.4	1284.6	1252.7	1221.3	1190.5	1161.3
25	1443.8	1409.6	1375.9	1343.5	1311.1	1279.6	1249.3	1219.5	1190.9
30	1466.9	1433.1	1399.9	1367.7	1336.8	1305.8	1276.2	1247.2	1219.2
35	1488.9	1455.4	1422.8	1391.7	1361.3	1330.8	1302.2	1273.8	1246.2
40	1509.9	1477.4	1446.1	1415.0	1384.7	1355.0	1327.0	1298.9	1272.5
45	1530.8	1498.5	1467.7	1437.1	1407.6	1378.4	1351.8	1323.6	1297.2
50	1550.7	1519.1	1488.0	1458.5	1429.8	1401.3	1374.2	1346.9	1321.3
55	1570.2	1539.0	1509.1	1479.6	1451.0	1423.1	1396.4	1370.0	1344.3
60	1589.4	1558.5	1528.7	1500.0	1471.8	1444.3	1418.3	1392.1	1367.2
65	1607.9	1577.3	1548.3	1520.2	1492.0	1465.0	1439.2	1413.5	1389.1
70	1625.9	1595.7	1567.4	1539.4	1512.0	1485.1	1459.8	1434.3	1410.2
75	1643.7	1614.4	1586.1	1558.3	1530.9	1504.8	1479.5	1454.8	1430.8
80	1660.5	1631.9	1603.8	1576.6	1549.4	1523.7	1498.8	1474.8	1451.0
85	1677.5	1649.3	1621.7	1594.6	1567.9	1542.2	1517.7	1494.0	1470.7
90	1694.2	1666.1	1639.0	1612.1	1585.7	1560.3	1536.3	1512.6	1489.4
95	1710.6	1682.5	1655.8	1629.3	1603.2	1577.8	1554.4	1530.7	1508.4
100	1726.9	1699.2	1672.4	1646.0	1620.2	1595.3	1572.1	1548.9	1526.5
105	1742.5	1715.3	1688.4	1662.5	1637.1	1612.1	1589.3	1566.6	1544.1
110	1758.1	1730.6	1704.3	1678.9	1653.6	1629.0	1605.9	1583.9	1561.5
115	1773.1	1746.0	1720.1	1694.4	1669.4	1645.4	1622.8	1600.4	1578.7
120	1787.9	1761.0	1735.3	1710.2	1685.6	1661.4	1639.2	1616.9	1595.4
125	1802.2	1775.8	1750.6	1725.4	1701.0	1677.0	1655.1	1633.2	1611.7
130	1816.8	1790.4	1765.0	1740.9	1716.5	1692.7	1671.0	1649.2	1627.6
135	1831.1	1805.0	1779.8	1755.4	1731.2	1707.6	1686.1	1664.6	1643.5
140	1844.7	1818.7	1794.3	1770.1	1746.4	1723.0	1701.5	1680.2	1659.0
145	1858.5	1833.0	1808.3	1784.4	1760.7	1737.6	1716.2	1694.5	1674.1
150	1872.2	1846.6	1822.2	1798.2	1774.8	1752.3	1730.9	1709.7	1689.1

linking isothermal and adiabatic compressibility coefficients, i.e.:

$$k_T = k_S + \frac{T\alpha_P^2}{\rho C_P} \tag{4}$$

(in which α_P designates the isobaric expansion coefficient and C_P the heat capacity at constant pressure), it is possible, replacing the product ρk_S by $1/u^2$, to express variation of density versus pressure in terms of the speed of sound:

$$\left(\frac{\partial \rho}{\partial P}\right)_T = \frac{1}{u^2} + \frac{T\alpha_P^2}{C_P} \tag{5}$$

which provides, by integrating with pressure, at a fixed temperature between a reference value P_o and an arbitrary value P, the relationship:

$$\rho(P,T) = \rho(P_0,T) + \int_{P_0}^{P} u^{-2} dP + T \int_{P_0}^{P} (\alpha_P^2/C_P) dP \qquad (6)$$

This relation can be used to calculate the density of the fluid at a given P, T condition on the basis of its value at conditions, P_0, T. This expression involves calculating the sum of three contributions. The first, which represents the main contribution, is directly deduced from additional density measurements performed at atmospheric pressure between 293.15 K and 373.15 K in 10 K steps and smoothed as a function of temperature using a third degree polynomial:

$$\rho(P_0,T) = \rho_0 + \rho_1 T + \rho_2 T^2 + \rho_3 T^3 \qquad (7)$$

the coefficients of which are displayed in Table VI. This representation introduces an average absolute deviation less than 0.005% with respect to the complete set of experimental data. The second contribution, whose corrective contribution is much more significant than that of the third, can be evaluated by means of the ultrasonic velocity measurements carried out along the isotherms considered. The third term can be determined by iterative calculation using the method proposed by Davis et Gordon [25] in which the behaviours of α_P and C_P versus pressure can be described by means of the thermodynamic relationships:

TABLE VI Parameters of the Equation (7) and Equations (11) to (13) and with T in K, P in MPa, ρ in Kg. m^{-3} and u in $\mathrm{m{\cdot}s}^{-1}$

*S*1		*S*2	
$\rho_0 = 1.22295.\ 10^{+03}$	$A_0 = -3.47530{\cdot}10^{-08}$	$\rho_0 = 1.0830{\cdot}10^{+03}$	$A_0 = -1.17840{\cdot}10^{-08}$
$\rho_1 = -2.68565$	$A_1 = 1.38426{\cdot}10^{-09}$	$\rho_1 = -1.4789$	$A_1 = 1.30791{\cdot}10^{-09}$
$\rho_2 = 5.93427 \cdot 10^{-03}$	$A_2 = -1.11780{\cdot}10^{-12}$	$\rho_2 = 2.3666{\cdot}10^{-03}$	$A_2 = -1.10340{\cdot}10^{-12}$
$\rho_3 = -6.23740 \cdot 10^{-06}$	$B = 1.48357{\cdot}10^{-09}$	$\rho_3 = -2.5589{\cdot}10^{-06}$	$B = 1.36053{\cdot}10^{-09}$
	$C = -4.45970{\cdot}10^{-12}$		$C = -3.86010{\cdot}10^{-12}$
	$D = 8.62982{\cdot}10^{-15}$		$D = 7.21970{\cdot}10^{-15}$
	$E_1 = -1.81292{\cdot}10^{-03}$		$E_1 = -1.77584{\cdot}10^{-03}$
	$F = 6.77730{\cdot}10^{-03}$		$F = 6.58071{\cdot}10^{-03}$

$$\left(\frac{\partial \alpha_P}{\partial P}\right)_T = -\left(\frac{\partial k_T}{\partial T}\right)_P \tag{8}$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -\frac{T}{\rho}\left\{\alpha_P^2 + \left(\frac{\partial \alpha_P}{\partial T}\right)_P\right\} \tag{9}$$

Consequently, this general procedure can extend the domain in which density can be determined to the entire pressure domain investigated during ultrasonic velocity measurement. However, before this numerical method can be applied, it is necessary to adopt analytical representations correlating the ultrasonic velocity data and the P and T parameters. This smoothing is necessary to evaluate the derivatives with respect to T (on ρ, α_P and especially k_T), unless a very small experimental increment ΔT is adopted, but in that case the number of experimental measurements which would have to be done would become prohibitive. To achieve this, polynomial forms of the type:

$$u = \sum_{i=0}^{n}\sum_{j=0}^{m} a_{ij} T^i P^j \tag{10}$$

in which n and m can have the values 3 or 4 have often been used [8, 26]. These correlations are indeed very accurate and allow reliable extrapolations of the property. However, as they involve 15 or 20 adjustable parameters depending on whether n or m are allocated the value 3 or 4, they generate complicated analytical forms for the integral of $1/u^2$. It is therefore preferable to correlate $1/u^2$ directly with the P and T parameters. While the dependency of this quantity as a function of P at fixed temperature can be reproduced using a polynomial form [17], using a polynomial form to represent both the P and T parameters simultaneously requires a large number of adjusted parameters to achieve a satisfactory degree of accuracy. For this reason we preferred a rational fonction whose denominator is of the first degree in P and T and which involves in all no more than 8 adjustable parameters, the values of which are presented in Table VI:

$$\frac{1}{u^2} = \frac{A + BP + CP^2 + DP^3}{E + FP} \tag{11}$$

with

$$A = A_0 + A_1 T + A_2 T^2 \tag{12}$$

$$E = 1 + E_1 T \tag{13}$$

The absolute average deviation observed between the predictions for this smoothing function and the complete set of experimental data, for each of the systems studied, is 0.02%. Moreover comparison of the standard deviations and absolute standard deviations shows that the formulation adopted does not introduce any systematic error on calculation of the ultrasonic velocity. The advantage of this representation lies in the simple analytic form of the integral of $1/u^2$ which is presented as follows:

$$\begin{aligned}\int u^{-2} dP = &\left(\frac{B}{F} - \frac{CE}{F^2} + \frac{DE^2}{F^3}\right) P + \left(\frac{C}{F} - \frac{DE}{F^2}\right)\frac{P^2}{2} + \left(\frac{D}{F}\right)\frac{P^3}{3} \\ &+ \left(\frac{A}{F} - \frac{BE}{F^2} + \frac{CE^2}{F^3} - \frac{DE^3}{F^4}\right)\ln(E + FP)\end{aligned} \tag{14}$$

It should be recalled that this quantity represents the predominant factor in density variation caused by changing pressure.

Thus the temperature increment used in the numeric procedure is no longer imposed by the experimental protocol (i.e. 10 K) but is fixed in such a way as to limit as far as possible the uncertainty due to derivations with respect to T. The incremental step chosen was 1 K, after numerous tests proved that the results were not affected by an increment less than $\Delta T = 3\,\mathrm{K}$. Consequently, each isobaric curve is defined by approximately a hundred points. Moreover, an approach of the "predictor corrector" type was preferred to use of the Equation (6) to generate the effect of pressure on the isobaric expansivity α_P [27, 28]. This iterative approach consists initially in estimating the variation of density ρ over a small interval ΔP considering the quantity $\alpha_P^2 T / C_P$:

$$\rho(P + \Delta P, T) - \rho(P_0, T) = \int_{P_0}^{P} u^{-2} dP + \frac{T\alpha_P^2}{C_P}\Delta P \tag{15}$$

to be constant, following Denielou *et al.* [29] and deducing from this by derivation the coefficient $\alpha_P(T)$ at $P + \Delta P$. The values obtained for

$\rho(T)$ and $\alpha_P(T)$ at pressure $P+\Delta P$ are then corrected by recalculating the value of ρ at $P+\Delta P$ using Equation (6) in which the behaviour of the coefficient α_P with pressure is interpolated linearly over the interval from the known values at P and the estimated values at $P+\Delta P$. During this integration, the heat capacity C_P is assimilated to a constant. The corrective process is then repeated until the values of ρ, calculated at $P+\Delta P$, remain fixed. Once this objective has been achieved, the value of C_P at $P+\Delta\ P$ is then calculated from Equation (9) taken in its integrated form. In all, referring to the ρ measurements carried out at atmospheric pressure only as well as to those of C_P performed at atmospheric pressure by Bessieres *et al.* [30], determination of density is extended by this procedure up to 150 MPa by means of the ultrasonic velocities $u(T, P)$.

Thus one has the advantage of obtaining the values of the compressibility coefficients k_S et k_T at the different pressures and temperatures studied in the investigation. Tables VII to XII present respectively the values obtained on each of the ternary systems for density, isentropic compressibility k_S and isothermal compressibility k_T. As an example we present in Figure 6 the bundles of isothermal and isobaric curves u (ρ). Figures 7 and 8 reflect the influence of temperature on the coefficients k_S and k_T. It would appear from

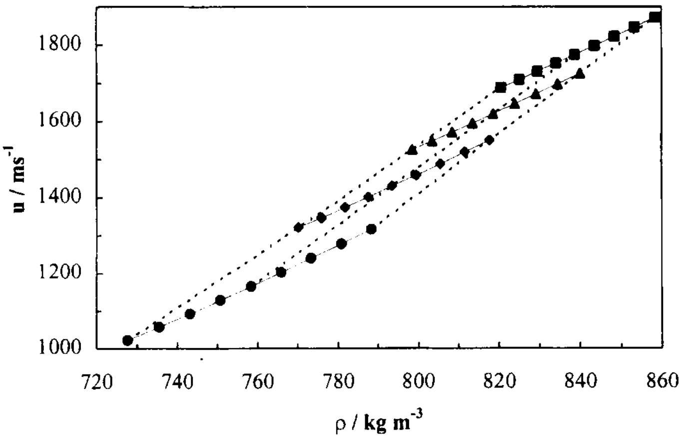

FIGURE 6 Speed of sound u in S2 as a function of density ρ. ● - : 0.1 MPa; -◆-: 50 MPa; -▲-: 100 MPa;- ■- : 150 MPa; ... : Isotherm curves.

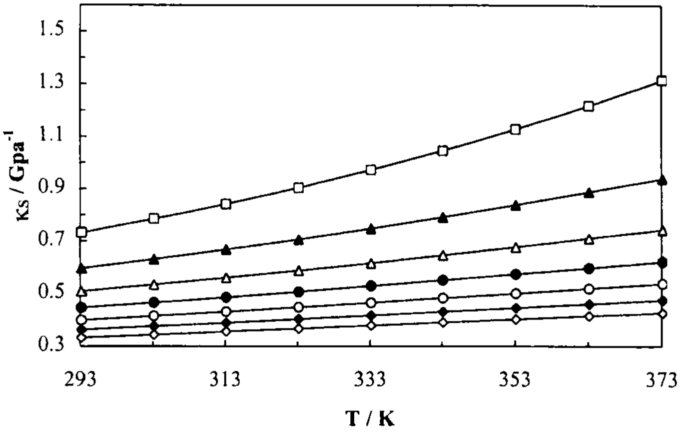

FIGURE 7 Isentropic compressibility κ_s in S2 as a function of temperature. -□- : 0.1 MPa; -▲- : 25 MPa; -△- : 50 MPa; -●- : 75 MPa; -○- : 100 MPa; -◆- : 125 MPa; -◇- : 0.150 MPa.

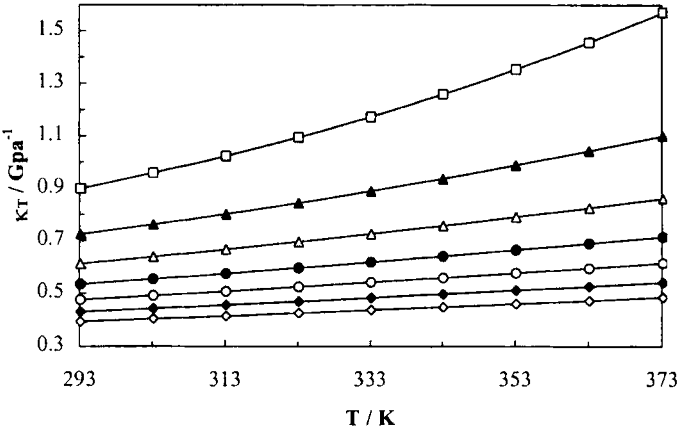

FIGURE 8 Isothermal compressibility κ_T in S2 as a function of temperature. -□- : 0.1 MPa; -▲- : 25 MPa; -△- : 50 MPa; -●- : 75 MPa; -○- : 100 MPa; -◆- : 125 MPa; -◇- : 150 MPa.

looking at these curves that the two compressibility coefficients have very similar behaviours, reflecting in particular a quasi-linear dependency on temperature at high pressure. At the highest pressures, of the order of 100 MPa or more, this dependency is even zero and the coefficients k_S and k_T are essentially constants.

TABLE VII Densities ρ (in Kg·m ^{3}) of S1 at temperatures T and pressures P

					T/K				
P/Mpa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
0.1	788.49	780.38	772.33	764.29	756.23	748.11	739.89	731.54	723.01
5	792.06	784.15	776.31	768.51	760.70	752.87	744.96	736.96	728.83
10	795.55	787.82	780.17	772.58	765.01	757.43	749.81	742.11	734.32
15	798.90	791.32	783.85	776.45	769.08	761.73	754.35	746.93	739.43
20	802.12	794.69	787.37	780.14	772.96	765.81	758.65	751.46	744.22
25	805.23	797.93	790.75	783.67	776.66	769.69	762.72	755.75	748.74
30	808.23	801.05	794.00	787.06	780.20	773.39	766.61	759.82	753.02
35	811.14	804.06	797.14	790.33	783.60	776.94	770.31	763.70	757.08
40	813.96	706.98	800.17	793.47	786.88	780.35	773.87	767.41	760.96
45	816.70	809.81	803.10	796.51	790.03	783.63	777.28	770.97	764.66
50	819.36	812.56	805.94	799.45	793.08	786.79	780.57	774.38	768.22
55	821.95	815.24	808.70	802.30	796.03	789.85	783.74	777.67	771.64
60	824.48	817.84	811.38	805.07	798.89	792.81	786.80	780.85	774.93
65	826.95	820.37	813.99	807.76	801.66	795.67	789.76	783.92	778.11
70	829.36	822.85	816.53	810.38	804.36	798.46	792.64	786.89	781.18
75	831.71	825.26	819.01	812.93	806.99	801.16	795.43	789.77	784.16
80	834.02	827.62	821.43	815.41	809.54	803.79	798.14	792.56	787.04
85	836.27	829.93	823.79	817.84	812.03	806.35	800.78	795.28	789.84
90	838.48	832.19	826.10	820.21	814.46	808.85	803.34	797.92	792.56
95	840.65	834.40	828.37	822.52	816.84	811.29	805.85	800.49	795.21
100	842.77	836.57	830.58	824.79	819.16	813.67	808.29	803.00	797.79
105	844.86	838.69	832.75	827.01	821.43	815.99	810.68	805.45	800.31
110	846.91	840.78	834.88	829.18	823.65	818.27	813.01	807.84	802.76
115	848.92	842.82	836.96	831.31	825.83	820.50	815.29	810.18	805.16
120	850.90	844.84	839.01	833.40	827.96	822.68	817.52	812.46	807.50
125	852.85	846.81	841.02	835.45	830.05	824.81	819.70	814.70	809.79
130	854.76	848.76	843.00	837.46	832.10	826.91	821.84	816.89	812.03
135	856.65	850.67	844.94	839.44	834.12	828.96	823.94	819.04	814.22
140	858.50	852.55	846.85	841.38	836.10	830.98	826.00	821.14	816.38
145	860.33	854.40	848.73	843.29	838.05	832.97	828.03	823.21	818.49
150	862.14	856.23	850.59	845.17	839.96	834.91	830.01	825.23	820.56

TABLE VIII Densities ρ (in Kg·m^{-3}) of S2 at temperatures T and pressures P

					T/K				
P/Mpa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
0.1	788.39	780.89	773.40	765.90	758.37	750.81	743.19	735.51	727.74
5	791.79	784.48	777.19	769.90	762.61	755.30	747.95	740.57	733.12
10	795.12	787.97	780.87	773.78	766.70	759.61	752.51	745.39	738.23
15	798.31	791.32	784.38	777.47	770.58	763.70	756.81	749.92	743.01
20	801.38	794.54	787.75	781.00	774.28	767.58	760.89	754.20	747.51
25	804.34	797.63	790.98	784.38	777.81	771.28	764.76	758.26	751.76
30	807.21	800.62	794.10	787.63	781.20	774.82	768.46	762.12	755.80
35	809.98	803.51	797.10	790.76	784.46	778.21	771.99	765.81	759.65
40	812.67	806.30	800.01	793.78	787.60	781.48	775.39	769.34	763.33
45	815.28	809.01	802.82	796.70	790.63	784.62	778.66	772.74	766.85
50	817.82	811.64	805.55	799.52	793.56	787.66	781.81	776.00	770.24
55	820.29	814.20	808.19	802.26	796.40	790.60	784.85	779.15	773.50

TABLE VIII (Continued)

					T/K				
P/Mpa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
60	822.70	816.69	810.77	804.92	799.15	793.44	787.79	782.20	776.65
65	825.05	819.12	813.27	807.51	801.83	796.21	790.65	785.14	779.69
70	827.35	821.48	815.72	810.03	804.42	798.89	793.41	788.00	782.64
75	829.59	823.79	818.10	812.49	806.95	801.49	796.10	790.77	785.49
80	831.78	826.05	820.42	814.88	809.42	804.03	798.71	793.46	788.26
85	833.93	828.26	822.69	817.22	811.82	806.51	801.26	796.08	790.95
90	836.03	830.42	824.91	819.50	814.17	808.92	803.74	798.62	793.57
95	838.08	832.53	827.08	821.73	816.46	811.27	806.16	801.11	796.12
100	840.10	834.60	829.21	823.91	818.70	813.57	808.52	803.53	798.61
105	842.08	836.63	831.29	826.05	820.89	815.82	810.82	805.90	801.04
110	844.02	838.62	833.33	828.14	823.04	818.02	813.08	808.21	803.41
115	845.93	840.58	835.34	830.19	825.14	820.18	815.29	810.47	805.72
120	847.80	842.50	837.30	832.21	827.20	822.29	817.45	812.68	807.98
125	849.65	844.38	839.23	834.18	829.23	824.35	819.56	814.85	810.20
130	851.46	846.24	841.13	836.12	831.21	826.38	821.64	816.97	812.37
135	853.24	848.06	842.99	838.02	833.16	828.37	823.67	819.05	814.49
140	854.99	849.85	844.82	839.90	835.07	830.33	825.67	821.09	816.58
145	856.72	851.61	846.62	841.74	836.95	832.25	827.63	823.09	818.62
150	858.42	853.35	848.39	843.55	838.80	834.14	829.56	825.06	820.63

TABLE IX Isentropic Compressibility κ_s (GPa^{-1}) of S1 as a function of pressure *P* and temperature *T*

					T/K				
P/Mpa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
0.1	0.7441	0.8006	0.8635	0.9329	1.0079	1.0903	1.1823	1.2839	1.3956
5	0.7096	0.7613	0.8178	0.8790	0.9458	1.0176	1.0984	1.1855	1.2790
10	0.6779	0.7261	0.7776	0.8327	0.8919	0.9578	1.0265	1.1030	1.1846
15	0.6514	0.6943	0.7415	0.7916	0.8453	0.9032	0.9654	1.0323	1.1055
20	0.6262	0.6662	0.7100	0.7549	0.8038	0.8558	0.9119	0.9718	1.0357
25	0.6033	0.6402	0.6807	0.7222	0.7667	0.8141	0.8651	0.9189	0.9760
30	0.5823	0.6167	0.6541	0.6929	0.7340	07772	0.8232	0.8725	0.9237
35	0.5629	0.5955	0.6295	0.6660	0.7047	0.7437	0.7860	0.8308	0.8776
40	0.5452	0.5754	0.6076	0.6417	0.6767	0.7140	0.7524	0.7938	0.8366
45	0.5285	0.5572	0.5876	0.6187	0.6520	0.6862	0.7217	0.7606	0.7996
50	0.5128	0.5399	0.5686	0.5978	0.6287	0.6607	0.6950	0.7303	0.7666
55	0.4985	0.5240	0.5510	0.5786	0.6073	0.6380	0.6697	0.7021	0.7359
60	0.4848	0.5093	0.5347	0.5607	0.5879	0.6166	0.6459	0.6770	0.7090
65	0.4721	0.4955	0.5196	0.5443	0.5699	0.5970	0.6247	0.6527	0.6827
70	0.4600	0.4825	0.5052	0.5290	0.5529	0.5784	0.6047	0.6314	0.6591
75	0.4481	0.4700	0.4918	0.5143	0.5373	0.5614	0.5858	0.6110	0.6375
80	0.4383	0.4586	0.4791	0.5006	0.5228	0.5453	0.5685	0.5925	0.6174
85	0.4284	0.4474	0.4671	0.4876	0.5088	0.5305	0.5525	0.5751	0.5985
90	0.4188	0.4373	0.4553	0.4754	0.4955	0.5160	0.5372	0.5589	0.5807
95	0.4093	0.4273	0.4453	0.4637	0.4831	0.5027	0.5225	0.5435	0.5645
100	0.4010	0.4182	0.4354	0.4535	0.4713	0.4903	0.5094	0.5290	0.5489
105	0.3928	0.4088	0.4261	0.4430	0.4596	0.4786	0.4968	0.5154	0.5340

TABLE IX (Continued)

	T/K								
P/Mpa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
110	0.3849	0.4008	0.4167	0.4333	0.4496	0.4674	0.4847	0.5026	0.5205
115	0.3773	0.3928	0.4080	0.4239	0.4399	0.4569	0.4730	0.4904	0.5077
120	0.3701	0.3855	0.3999	0.4149	0.4307	0.4465	0.4630	0.4791	0.4956
125	0.3634	0.3773	0.3919	0.4067	0.4217	0.4370	0.4526	0.4683	0.4837
130	0.3566	0.3704	0.3842	0.3986	0.4132	0.4277	0.4427	0.4577	0.4733
135	0.3503	0.3636	0.3772	0.3910	0.4048	0.4187	0.4333	0.4479	0.4621
140	0.3444	0.3571	0.3702	0.3836	0.3970	0.4106	0.4240	0.4384	0.4526
145	0.3384	0.3508	0.3634	0.3765	0.3893	0.4025	0.4158	0.4297	0.4432
150	0.3329	0.3448	0.3572	0.3698	0.3821	0.3950	0.4079	0.4213	0.4342

TABLE X Isentropic Compressibility κ_s (GPa^{-1}) of S2 as a function of pressure P and temperature T

	T/K								
P/Mpa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
0.1	0.7316	0.7844	0.8407	0.9033	0.9720	1.0465	1.1280	1.2167	1.3146
5	0.6993	0.7472	0.7985	0.8547	0.9157	0.9815	1.0523	1.1293	1.2127
10	0.6694	0.7133	0.7605	0.8110	0.8653	0.9242	0.9871	1.0549	1.1277
15	0.6429	0.6835	0.7257	0.7722	0.8218	0.8745	0.9306	0.9907	1.0547
20	0.6186	0.6558	0.6951	0.7378	0.7827	0.8303	0.8811	0.9355	0.9920
25	0.5964	0.6310	0.6678	0.7063	0.7479	0.7918	0.8378	0.8867	0.9378
30	0.5757	0.6081	0.6425	0.6787	0.7163	07569	0.7989	0.8436	0.8901
35	0.5569	0.5875	0.6197	0.6529	0.6879	0.7255	0.7639	0.8048	0.8477
40	0.5398	0.5682	0.5978	0.6292	0.6622	0.6970	0.7323	0.7704	0.8090
45	0.5235	0.5504	0.5783	0.6077	0.6384	0.6708	0.7028	0.7386	0.7749
50	0.5085	0.5339	0.5607	0.5880	0.6164	0.6465	0.6774	0.7104	0.7437
55	0.4944	0.5185	0.5433	0.5693	0.5964	0.6246	0.6534	0.6838	0.7154
60	0.4812	0.5041	0.5278	0.5522	0.5776	0.6042	0.6310	0.6597	0.6889
65	0.4688	0.4907	0.5130	0.5358	0.5603	0.5852	0.6106	0.6374	0.6647
70	0.4572	0.4781	0.4990	0.5210	0.5438	0.5675	0.5914	0.6169	0.6425
75	0.4462	0.4658	0.4859	0.5069	0.5287	0.5510	0.5739	0.5975	0.6219
80	0.4360	0.4546	0.4739	0.4937	0.5146	0.5357	0.5573	0.5795	0.6026
85	0.4261	0.4438	0.4622	0.4812	0.5011	0.5213	0.5418	0.5628	0.5845
90	0.4167	0.4338	0.4513	0.4695	0.4885	0.5078	0.5272	0.5473	0.5681
95	0.4078	0.4243	0.4410	0.4585	0.4765	0.4951	0.5134	0.5327	0.5521
100	0.3991	0.4150	0.4312	0.4480	0.4653	0.4830	0.5004	0.5187	0.5374
105	0.3911	0.4063	0.4220	0.4380	0.4545	0.4717	0.4883	0.5056	0.5236
110	0.3833	0.3982	0.4131	0.4284	0.4444	0.4607	0.4769	0.4932	0.5105
115	0.3760	0.3903	0.4046	0.4196	0.4349	0.4504	0.4658	0.4817	0.4980
120	0.3690	0.3828	0.3966	0.4109	0.4255	0.4406	0.4553	0.4707	0.4862
125	0.3624	0.3756	0.3888	0.4027	0.4168	0.4313	0.4454	0.4601	0.4752
130	0.3558	0.3687	0.3816	0.3946	0.4083	0.4223	0.4359	0.4500	0.4647
135	0.3495	0.3619	0.3745	0.3873	0.4005	0.4140	0.4270	0.4406	0.4545
140	0.3437	0.3558	0.3677	0.3800	0.3927	0.4057	0.4183	0.4314	0.4450
145	0.3380	0.3495	0.3612	0.3731	0.3854	0.3980	0.4102	0.4231	0.4359
150	0.3323	0.3437	0.3550	0.3666	0.3785	0.3905	0.4024	0.4147	0.4271

TABLE XI Isothermal Compressibility κ_T (GPa^{-1}) of S1 as a function of pressure P and temperature T

	T/K								
P/Mpa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
0.1	0.9464	1.0083	1.0785	1.1574	1.2446	1.3421	1.4526	1.5767	1.7156
5	0.9004	0.9560	1.0182	1.0870	1.1636	1.2476	1.3434	1.4486	1.5638
10	0.8584	0.9093	0.9651	1.0263	1.0934	1.1692	1.2500	1.3413	1.4405
15	0.8228	0.8675	0.9180	0.9728	1.0328	1.0988	1.1711	1.2501	1.3377
20	0.7895	0.8305	0.8766	0.9253	0.9792	1.0379	1.1023	1.1723	1.2483
25	0.7594	0.7966	0.8386	0.8829	0.9316	0.9845	1.0424	1.1046	1.1718
30	0.7318	0.7661	0.8044	0.8453	0.8896	0.9373	0.9890	1.0455	1.1052
35	0.7065	0.7385	0.7728	0.8108	0.8520	0.8947	0.9418	0.9927	1.0467
40	0.6834	0.7125	0.7447	0.7797	0.8166	0.8569	0.8994	0.9459	0.9950
45	0.6618	0.6890	0.7190	0.7505	0.7853	0.8218	0.8607	0.9041	0.9485
50	0.6416	0.6670	0.6948	0.7241	0.7559	0.7899	0.8270	0.8660	0.9069
55	0.6233	0.6466	0.6726	0.6999	0.7291	0.7613	0.7954	0.8308	0.8687
60	0.6057	0.6279	0.6519	0.6774	0.7048	0.7346	0.7658	0.7995	0.8351
65	0.5895	0.6104	0.6328	0.6567	0.6822	0.7101	0.7393	0.7695	0.8026
70	0.5741	0.5939	0.6148	0.6374	0.6611	0.6870	0.7145	0.7430	0.7734
75	0.5591	0.5782	0.5979	0.6191	0.6416	0.6659	0.6912	0.7180	0.7467
80	0.5465	0.5638	0.5821	0.6021	0.6235	0.6460	0.6698	0.6952	0.7220
85	0.5539	0.5498	0.5671	0.5859	0.6062	0.6277	0.6501	0.6738	0.6988
90	0.5219	0.5371	0.5525	0.5708	0.5898	0.6099	0.6314	0.6538	0.6770
95	0.5101	0.5246	0.5400	0.5565	0.5746	0.5936	0.6134	0.6351	0.6572
100	0.4996	0.5133	0.5277	0.5437	0.5601	0.5784	0.5974	0.6174	0.6383
105	0.4894	0.5016	0.5161	0.5308	0.5459	0.5640	0.5819	0.6008	0.6202
110	0.4796	0.4917	0.5045	0.5189	0.5335	0.5503	0.5672	0.5883	0.6038
115	0.4701	0.4818	0.4939	0.5074	0.5217	0.5375	0.5531	0.5705	0.5883
120	0.4611	0.4726	0.4839	0.4964	0.5104	0.5250	0.5408	0.5567	0.5736
125	0.4528	0.4628	0.4741	0.4863	0.4994	0.5134	0.5283	0.5437	0.5594
130	0.4445	0.4543	0.4647	0.4765	0.4891	0.5021	0.5163	0.5310	0.5466
135	0.4368	0.4459	0.4561	0.4672	0.4789	0.4913	0.5050	0.5191	0.5334
140	0.4295	0.4380	0.4476	0.4582	0.4694	0.4815	0.4939	0.5078	0.5219
145	0.4222	0.4303	0.4394	0.4496	0.4602	0.4718	0.4839	0.4972	0.5106
150	0.4154	0.4230	0.4318	0.4415	0.4515	0.4627	0.4744	0.4872	0.4998

TABLE XII Isothermal Compressibility κ_T (GPa^{-1}) of S2 as a function of pressure P and temperature T

	T/K								
P/Mpa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
0.1	0.9001	0.9597	1.0236	1.0949	1.1736	1.2593	1.3535	1.4566	1.5709
5	0.8580	0.9115	0.9693	1.0327	1.1019	1.1768	1.2580	1.3465	1.4429
10	0.8193	0.8678	0.9204	0.9769	1.0380	1.1045	1.1758	1.2530	1.3362
15	0.7848	0.8294	0.8761	0.9276	0.9830	1.0419	1.1051	1.1728	1.2452
20	0.7534	0.7940	0.8370	0.8840	0.9337	0.9866	1.0432	1.1040	1.1674
25	0.7249	0.7623	0.8023	0.8444	0.8901	0.9384	0.9893	1.0435	1.1004
30	0.6985	0.7332	0.7703	0.8096	0.8506	0.8949	0.9411	0.9902	1.0415
35	0.6744	0.7070	0.7415	0.7773	0.8151	0.8560	0.8979	0.9425	0.9894
40	0.6525	0.6825	0.7141	0.7477	0.7832	0.8206	0.8590	0.9002	0.9422
45	0.6318	0.6601	0.6896	0.7209	0.7536	0.7884	0.8228	0.8614	0.9006

TABLE XII (Continued)

	T/K								
P/Mpa	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
50	0.6128	0.6393	0.6674	0.6963	0.7265	0.7585	0.7915	0.8268	0.8626
55	0.5950	0.6200	0.6459	0.6732	0.7017	0.7316	0.7622	0.7946	0.8282
60	0.5783	0.6019	0.6264	0.6519	0.6787	0.7066	0.7350	0.7653	0.7962
65	0.5627	0.5851	0.6081	0.6318	0.6573	0.6834	0.7102	0.7384	0.7671
70	0.5481	0.5693	0.5908	0.6135	0.6371	0.6619	0.6869	0.7135	0.7404
75	0.5343	0.5541	0.5746	0.5961	0.6187	0.6418	0.6656	0.6903	0.7157
80	0.5215	0.5401	0.5597	0.5800	0.6014	0.6232	0.6456	0.6686	0.6925
85	0.5092	0.5268	0.5454	0.5647	0.5850	0.6057	0.6269	0.6485	0.6710
90	0.4974	0.5144	0.5319	0.5504	0.5696	0.5893	0.6093	0.6299	0.6513
95	0.4863	0.5026	0.5193	0.5368	0.5551	0.5741	0.5927	0.6125	0.6323
100	0.4756	0.4912	0.5072	0.5241	0.5415	0.5594	0.5772	0.5958	0.6148
105	0.4656	0.4804	0.4959	0.5119	0.5285	0.5457	0.5626	0.5802	0.5985
110	0.4560	0.4704	0.4851	0.5003	0.5162	0.5326	0.5489	0.5654	0.5829
115	0.4469	0.4607	0.4747	0.4895	0.5047	0.5202	0.5357	0.5518	0.5682
120	0.4383	0.4515	0.4650	0.4789	0.4934	0.5084	0.5232	0.5386	0.5543
125	0.4301	0.4427	0.4555	0.4690	0.4830	0.4974	0.5114	0.5261	0.5412
130	0.4220	0.4342	0.4467	0.4593	0.4728	0.4866	0.5001	0.5142	0.5288
135	0.4143	0.4260	0.4380	0.4504	0.4634	0.4766	0.4896	0.5031	0.5169
140	0.4071	0.4184	0.4298	0.4417	0.4540	0.4668	0.4792	0.4922	0.5056
145	0.4000	0.4108	0.4220	0.4334	0.4453	0.4576	0.4696	0.4823	0.4949
150	0.3932	0.4037	0.4144	0.4255	0.4370	0.4486	0.4603	0.4724	0.4846

4. CONCLUSION

Despite the sustained attention devoted over a number of years to research on petroleum fluids, it is apparent that major shortcomings have been revealed in the experimental characterization of some of their components, especially the heavy components. This situation is a handicap to effective modelling of the heavy C_{11} + fractions and consequently to optimised production of these fluids. This explains the increasing number of investigations focusing on hydrocarbons with a high molecular weight and on asphaltenes.

Our contribution, concentrating on ternary systems which simulate distillation cuts belonging to the heavy fraction or located at the boundary between the heavy and lighter fractions is thus placed within this general perspective. The desired objective was to provide further experimental data obtained at high pressure and likely to improve our understanding of the exact role of the heavy fraction.

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