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Thermodynamic and acoustic properties of (heptane + dodecane) mixtures under elevated pressures

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ABSTRACT

The speed of sound in (heptane + dodecane) mixtures was measured over the whole concentration range at pressures up to 101 MPa and within the temperature range from (293 to 318) K. The density of (heptane + dodecane) was measured in the whole composition range under atmospheric pressure and at temperatures from (293 to 318) K. The densities and heat capacities of these binaries at the same temperatures were calculated for pressures up to 100 MPa from the speeds of sound under elevated pressures together with the densities and heat capacities at atmospheric pressure. The effects of pressure and temperature on the excess molar volume and the excess molar heat capacity are discussed.

1. Introduction

Normal paraffins, such as, for example, heptane and dodecane, are components of the fuels. Dodecane is used as a model of the "low or no sulphur" petrodiesel fuel [1]. Moreover, the thermodynamic properties of dodecane are similar to those of aviation kerosene [2].

For explanation the behaviour of multicomponent mixtures, such as fuels, investigations of model systems are required. The modeling of fuels requires the use of the mixtures with a limited number of components in order to represent the thermodynamic properties.

In an engine, the injection is an approximate adiabatic process rather than an isothermal one. Therefore, the isentropic compressibility is particularly useful in the estimation of fuel injection timing [3]. The only experimental method that leads directly to isentropic compressibility is the acoustic one, based on the measurement of the speed of sound. Furthermore, in modern common rail systems that issue is even more important since the pressure can reach 250 MPa instead of *ca.* 35 MPa.

Therefore, the petrochemical industry is interested in the thermodynamic and acoustic properties of binary alkane mixtures under elevated pressures.

Moreover, thermodynamic properties of (alkane + alkane) mixtures under high pressures are also of considerable interest from the theoretical point of view. Binary mixtures of alkanes are interesting systems for such investigations because the impact of pressure on the thermodynamic properties should be analyzed taking into account the effects of short-range orientational order, dispersion force interactions, and the packing of molecules (space filling effect).

Beside the direct determination of $p\rho T$, there is a competitive acoustic method based on the measurements of the speed of sound as function of temperature and pressure. Such properties as density and heat capacity can be calculated from the speed of sound in a thermodynamically exact way [4,5]. Sun *et al.* [5] claimed that the accuracy attained in the acoustic method is better than that of direct measurements. Bessières and Plantier [6] provided consistency between calorimetric, acoustic, and volumetric measurements under high pressures.

This work is a part of systematic studies of thermodynamic and acoustic properties of organic liquid mixtures under elevated pressures [3,7–10]. In this paper, the experimental densities and speeds of sound in the system (heptane + dodecane) are reported for the temperature range from (293 to 318) K at atmospheric and at pressures up to 101 MPa, respectively. Moreover, the densities and heat capacities of the system under test calculated for the pressures up to 100 MPa and over the temperature range from (293.15 to 318.15) K, by the above-mentioned acoustic method, are presented. To the best of our knowledge, these properties have never been investigated under elevated pressures.

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2. Experimental

The following chemicals have been used heptane (POCH [Polish Chemicals], analytically pure, minimum 0.99 mass fraction purity C_7H_{16}) and dodecane (Aldrich, 0.99+ mass fraction purity $C_{12}H_{26}$). The purities of these chemicals were tested by comparison of the refractive indexes, densities and speeds of sound with literature values (table 1).

The mixtures were prepared by weighing. The balance accuracy was $\pm 6 \cdot 10^{-4}$ g. Each sample was degassed in an ultrasonic cleaner just before the measurement.

The speed of sound in the pure components and in (heptane + dodecane) mixtures was measured at atmospheric and higher pressures using two measuring sets designed and constructed in our laboratory [27,28]. Two measuring vessels of the same acoustic paths and constructions have been used. One of them has been designed for the measurements under atmospheric pressure, the second one for elevated pressures. A single transmitting-receiving ceramic transducer operating at 2 MHz and an acoustic mirror were applied. The measuring sets operate on the principle of the pulse-echo-overlap method. The pressure was provided by a hand operated hydraulic press and was measured with a strain gauge measuring system (*Hottinger Baldwin System P3MD*) with an accuracy better than 0.15%. A stability of ±0.03 MPa during the measurement was achieved. The temperature has been measured using an *Ertco Hart 850* platinum resistance thermometer with an accuracy of ±0.05 K and resolution of 0.001 K. During the measurements, the stability of temperature was ±0.01 K. All temperatures reported in this work are expressed in the International Temperature Scale of 1990 (ITS-90).

Redistilled water was used as the standard for the calibration of the ultrasonic apparatus. Its electrolytic conductivity was $1 \cdot 10^{-4}\ \Omega^{-1} \cdot m^{-1}$. The speed of sound in water calculated from the polynomial of Marczak [29] at atmospheric pressure and from the Kell and Whalley [30] polynomial at higher pressures were taken as true values.

The repeatability of the measured speeds of sound was better than ±0.02% at atmospheric pressure and ±0.04% under elevated pressures. The uncertainties under atmospheric and elevated pressures were estimated to be better than $\pm 0.5\ m \cdot s^{-1}$ and $\pm 1\ m \cdot s^{-1}$, respectively. Other details of the high-pressure device and the method of the speed of sound measurements can be found in the previous papers [27,28].

The densities at atmospheric pressure were measured using the vibrating tube densimeter Anton Paar DMA 5000. The densimeter was calibrated with air and re-distilled water of electrolytic conductivity as above and degassed by boiling just before each measurement. The uncertainty of the density measurements was $0.05\ kg \cdot m^{-3}$, whereas the repeatability was estimated to be better than $0.005\ kg \cdot m^{-3}$.

3. Measurement results

The speed of sound was measured over the whole concentration range within the temperature limits from (293 to 318) K and under pressures varying from that of atmosphere up to 101 MPa. The measured speeds of sound at atmospheric pressure and under higher pressures are listed in tables 2 and 3, respectively.

TABLE 1
Comparison of the refractive index, density and speed of sound in the pure components at T = 298.15 K under atmospheric pressure obtained in this work with those reported in the literature

Component	This work	Literature
Heptane		
n_D	1.3853	1.3851 [11], 13852 [12,13], 1.3855 [14]
$\rho/(kg \cdot m^{-3})$	679.56	679.48 [15], 679.57 [16], 679.60 [17], 679.68 [7], 679.7 [18]
$u/(m \cdot s^{-1})$	1129.97	1129.85 [19], 1129.92 [7], 1130.1[18],1130.18 [17]
Dodecane		
n_D	1.4197	1.4195 [20], 1.4196 [12], 1.4198 [14]
$\rho/(kg \cdot m^{-3})$	745.28	745.2 [20], 745.23 [21], 745.25 [22], 745.3 [23]
$u/(m \cdot s^{-1})$	1278.86	1278.53 [24], 1278.91 [25], 1279 [23], 1284.5 [26]

TABLE 2
Speed of sound in {heptane (1) + dodecane (2)} mixtures within the temperature range (293 to 318) K at atmospheric pressure

x_1	T/K	$u/(m \cdot s^{-1})$	x_1	T/K	$u/(m \cdot s^{-1})$	x_1	T/K	$u/(m \cdot s^{-1})$
0.0000	292.89	1299.49	0.3002	313.11	1187.59	0.7002	303.15	1168.23
0.0000	298.16	1278.87	0.3002	318.39	1167.04	0.7002	308.13	1147.73
0.0000	303.15	1259.35	0.3996	292.89	1255.03	0.7002	313.11	1127.33
0.0000	308.12	1240.15	0.3996	298.18	1233.83	0.7002	318.38	1105.86
0.0000	313.10	1220.98	0.3996	303.16	1213.89	0.8000	292.90	1193.43
0.0000	318.39	1200.90	0.3996	308.14	1194.08	0.8000	298.17	1171.22
0.1007	292.91	1289.61	0.3996	313.11	1174.38	0.8000	303.16	1150.35
0.1007	298.18	1268.88	0.3996	318.39	1153.57	0.8000	308.13	1129.56
0.1007	303.16	1249.38	0.5002	292.91	1241.28	0.8000	313.12	1108.92
0.1007	308.15	1230.02	0.5002	298.18	1219.89	0.8000	318.40	1087.03
0.1007	313.14	1210.72	0.5002	303.16	1199.79	0.8995	292.89	1174.42
0.1007	318.40	1190.49	0.5002	308.15	1179.78	0.8995	298.16	1151.86
0.2001	292.91	1278.96	0.5002	313.13	1159.90	0.8995	303.14	1130.67
0.2001	298.19	1258.11	0.5002	318.41	1138.87	0.8995	308.12	1109.56
0.2001	303.17	1238.52	0.6000	292.89	1226.77	0.8995	313.10	1088.45
0.2001	308.15	1219.03	0.6000	298.16	1205.14	0.8995	318.38	1066.33
0.2001	313.13	1199.68	0.6000	303.14	1184.85	1.0000	292.83	1153.15
0.2001	318.41	1179.32	0.6000	308.12	1164.56	1.0000	298.12	1130.11
0.3002	292.89	1267.46	0.6000	313.10	1144.44	1.0000	303.10	1108.55
0.3002	298.16	1246.46	0.6000	318.37	1123.24	1.0000	308.08	1086.97
0.3002	303.15	1226.72	0.7002	292.89	1210.71	1.0000	313.06	1065.59
0.3002	308.13	1207.11	0.7002	298.17	1188.84	1.0000	318.35	1043.05