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ACOUSTIC AND THERMODYNAMIC PROPERTIES OF THE BINARY LIQUID SYSTEM *n*-DODECANE+*n*-HEXADECANE

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By the method of direct measurement of the pulse-passage time, the velocity of sound in a binary liquid mixture n-dodecane+n-hexadecane has been investigated in the temperature range 298–433 K and in the pressure range 0.1–100.1 MPa. The maximum measurement error is 0.1%. Experimental data on the velocity of sound for the investigated mixture have been obtained for the first time. On the basis of the data on the velocity of sound, we have determined the density, the isobaric expansion coefficient, the isobaric and isochoric heat capacities, and the isothermal compressibility coefficient of a mixture of three compositions in the 298–433 K temperature range and in the 0.1–100.1 MPa range of pressures. The coefficients of the Tate equations in the above range of parameters have been calculated. A table of thermodynamic properties of the mixture is presented.

Keywords: *n-dodecane, n-hexadecane, binary mixtures, velocity of sound, density, heat capacity, compressibility, isobaric expansion coefficient.*

Introduction. The present work is a sequel to our investigations [1–3] of the thermodynamic properties of liquid *n*-alkanes (C_nH_{2n+2}) and their mixtures in a wide range of temperatures and pressures by the acoustic method. The method is based on the use of the velocity of sound as the basic thermodynamic parameter in calculating and matching the thermodynamic properties in a liquid. It should be noted that the acoustic and thermodynamic properties of liquid mixtures of *n*-alkanes, including binary mixtures, are still not clearly understood. The investigations were carried out mainly at atmospheric pressure. At a higher pressure, there is only a small number of works in which the density and isobaric heat capacity for individual types and compositions of mixtures were measured. Noteworthily, the investigations were not systematic. Previously, the authors of [3] had measured the velocity of sound in binary liquid mixtures *n*-hexane+*n*-hexadecane, *n*-octane+*n*-hexadecane, and *n*-decane+*n*-hexadecane at temperatures of 298–433 K and pressures of up to 100 MPa. In the same work, an overview and analysis of experimental works devoted to measurements of the velocity of sound in mixtures of alkanes were given.

The present paper is devoted to the investigation of the velocity of sound in a binary liquid system *n*-dodecane+*n*-hexadecane ($C_{12} + C_{16}$) in the temperature range 298–433 K, pressure range 0.1–100.1 MPa, and at molar concentrations of *n*-dodecane of 0.25, 0.50, and 0.75, as well as to the determination of the thermodynamic properties of the mixture in the above range of parameters.

Experimental Data. Measurements of the velocity of sound were made on an experimental facility realizing the method of direct measurements of the time in which the acoustic pulse covers a known distance (sound-ranging base) in the investigated liquid [1, 3].

The main element of the facility is the measuring cell representing two parallel piezoelectronic ceramic plates from TsTS-19 of diameter 0.01 m with a resonance frequency of 3 MHz separated by a stainless steel tube. The time of passage of the acoustic pulse through the investigated medium was measured by a digital oscilloscope accurate to 0.01%. The cell is relieved from pressure and is placed in a high-pressure autoclave. Thermostating of the autoclave with the cell was carried out in a liquid thermostat. The temperature was measured by a platinum resistance thermometer accurate to 0.02 K, pressure measurements were taken by a dead-weight pressure-gauge tester of accuracy class 0.05. The length of the sound-ranging base was 0.49544 m at atmospheric pressure and a temperature of 298.15 K.

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TABLE 1. Experimental Values of the Velocity of Sound in the Binary Liquid Mixture *n*-dodecane+*n*-hexadecane (molar concentrations), m/s

T, K	p, MPa						
	0.1	10.1	20.1	40.1	60.1	80.1	100.1
			$0.25\ C_{12} + 0.75\ C_{16}$				
298.15	1327.0	1382.0	1432.6	—	—	—	—
333.15	1198.6	1261.2	1317.6	1417.6	1504.8	1583.0	1654.2
373.15	1062.1	1134.6	1198.6	1309.0	1403.7	1487.3	1562.8
393.15	997.3	1075.3	1143.3	1259.2	1357.4	1443.7	1521.3
433.15	873.3	964.1	1040.6	1167.5	1272.7	1364.1	1445.5
			$0.5\ C_{12} + 0.5\ C_{16}$				
298.15	1313.1	1369.1	1420.1	—	—	—	—
333.15	1184.5	1248.3	1305.7	1406.9	1495.3	1574.2	1645.9
373.15	1046.5	1120.7	1185.9	1298.1	1393.8	1478.4	1554.5
393.15	980.9	1060.8	1130.1	1247.8	1347.3	1434.6	1512.8
433.15	855.0	948.6	1026.8	1155.8	1262.4	1354.7	1436.7
			$0.75\ C_{12} + 0.25\ C_{16}$				
298.15	1297.5	1354.4	1406.4	—	—	—	—
333.15	1167.0	1232.1	1290.7	1393.6	1482.9	1562.6	1634.9
373.15	1027.4	1103.6	1170.2	1284.3	1381.4	1466.9	1543.8
393.15	960.9	1043.3	1114.1	1234.0	1334.9	1423.0	1501.9
433.15	833.0	930.1	1010.3	1141.8	1250.0	1343.4	1426.4

In calculating the experimental values, we allowed corrections for the change in the length of the sound-ranging base with temperature and pressure, for the diffraction, and for the waveguide effect. No sound velocity dispersion in the region of the investigated parameters was observed. The compositions of the mixtures were prepared by the weighting method. For the investigations, we used Aldrich alkane samples with a mass purity of the base product of over 99%.

According to our estimates, the error in determining the velocity of sound is 0.1%.

Measurements of the velocity of sound were made on five isomers: 298.15, 333.15, 373.15, 393.15, and 433.15 K in the 0.1–100.1 MPa range of pressures and at molar concentrations of 0.25, 0.50, and 0.75 of dodecane in the mixture. We obtained 93 values of the velocity of sound. In the investigated interval of parameters, data for the $C_{12} + C_{16}$ mixture were obtained for the first time. The experimental data are presented in Table 1.

The reproducibility of data on the velocity of sound obtained in the process of repeated measurements at various temperatures and pressures, including the initial temperature and atmospheric pressure, did not exceed 0.03%. To confirm the absence of pollutants and a change in the compositions of the investigated mixture $C_{12} + C_{16}$, we performed chromatographic analysis before and after measurements, which showed that their compositions remained unaltered.

The results of the analysis of the dependence of the velocity of sound in the dodecane+hexadecane mixture on the concentration at various temperatures and pressures suggest that the concentration dependence of the velocity of sound is nonlinear. The deviation of the velocity of sound ΔW in the mixture from the additivity rule was estimated by the molar concentration:

$$\Delta W = W - (x_1 W_1 + x_2 W_2)\ . \tag{1}$$

The calculations made have shown that the maximum deviation (0.6%) of the velocity of sound in the mixture from the corresponding additive values is observed at a temperature of 433.15 K, a pressure of 0.1 MPa, and a molar concentration of dodecane equal to 0.5. With increasing pressure at a constant temperature the deviation decreases and with increasing temperature at a constant pressure it increases.

Figure 1 shows the deviation of the velocity of sound for the investigated $C_{12} + C_{16}$ mixture depending on the concentration at a pressure of 0.1 MPa and a temperature of 333.15 K. For comparison, the same figure shows the

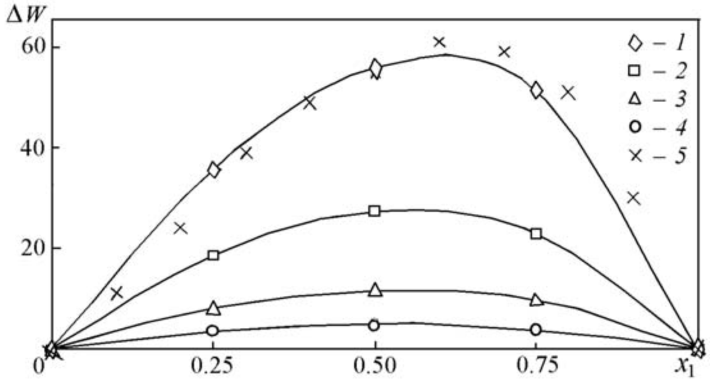

Fig. 1. Deviation of the velocity of sound in the alkane+hexadecane mixture at a pressure of 0.1 MPa and a temperature of 333.15 K: 1) hexane+hexadecane [3]; 2) octane+hexadecane [3]; 3) decane+hexadecane [3]; 4) dodecane+hexadecane (present paper); 5) hexane+hexadecane [4] (x_i is the molar concentration of alkane). ΔW, m/s.

TABLE 2. Parameters of Equations (2) and (3)

Parameter	x		
	0.25	0.5	0.75
E_0	0.05434	0.0547	0.05443
E_1	0.46124	0.4567	0.45843
E_2	6.4347	6.3741	6.2712
E_3	0.068198	0.069438	0.069897
e_0	0.074328	0.0646	0.06645
e_1	0.0224737	0.027906	0.029846
k	2.4	2.3	2.3
T_{cr}	707.7	692.4	675.8

deviations for the mixtures $C_6 + C_{16}$, $C_8 + C_{16}$, $C_{10} + C_{16}$ [3], and $C_6 + C_{16}$ [4]. As is seen, the deviation from the molar-additive rule will be the smaller the smaller the difference in mass and structure of the mixture components.

To calculate the thermodynamic properties of the mixture, the experimental data on the velocity of sound were approximated for each composition of the mixture depending on the temperature and pressure by the equation

$$\left(\frac{1000}{W}\right)^2 = E_0 + \frac{E_1}{E_2\left(\frac{T}{100}\right)^{-1.1} + \frac{p}{100}} + \frac{E_3\left(\frac{T}{100}\right)}{E_4 + \frac{p}{100}} . \tag{2}$$

The temperature dependence of E_4 has the form

$$E_4 = e_0 + e_1\left(\frac{T_{cr} - T}{100}\right)^k . \tag{3}$$

The critical temperature of the mixture was determined as follows. It is known that within the homological series of n-alkanes (excluding the lightest ones) the critical temperature, along with other thermodynamic properties, changes monotonically depending on the number of carbon atoms in the homolog or on the molar mass. We first calculated the average number of carbon atoms of components in the mixture as

TABLE 3. Coefficients of Equations (6) and (7)

Coefficients	x				
	0 [2]	0.25	0.5	0.75	1
a_0	410.701	411.332	413.23	415.056	416.283
a_1	1.13071	1.16531	1.19062	1.21886	1.25263
a_2	$-9.5509\cdot10^{-4}$	–10.5836·10–4	$-11.3937\cdot10^{-4}$	$-12.327\cdot10^{-4}$	$-13.4743\cdot10^{-4}$
a_3	$6.7842\cdot10^{-7}$	7.8582·10–7	$8.78717\cdot10^{-7}$	$9.9057\cdot10^{-7}$	11.3391·10–7
c_0	8.7527	6.6586	6.5644	6.4459	6.4315
c_1	$-77.7203\cdot10^{-3}$	–55.726·10–3	$-54.508\cdot10^{-3}$	$-53.4545\cdot10^{-3}$	–53.494·10–3
c_2	$0.328054\cdot10^{-3}$	0.24298·10–3	$0.236717\cdot10^{-3}$	$0.232954\cdot10^{-3}$	$0.233504\cdot10^{-3}$
c_3	$-5.92853\cdot10^{-7}$	–4.5048·10–7	$-4.3637\cdot10^{-7}$	$-4.30138\cdot10^{-7}$	$-4.31466\cdot10^{-7}$
c_4	$4.0297\cdot10^{-10}$	$3.17325\cdot10^{-10}$	$3.061059\cdot10^{-10}$	$3.0255\cdot10^{-10}$	3.0405·10–10
T_{cr}	722.0	707.7	692.4	675.8	658.0

$$N = x_1 N_1 + x_2 N_2 \,. \tag{4}$$

Then we calculated T_{cr} by the equation proposed in [5]:

$$T_{\mathrm{cr}} = 1426.4 - 4086.3 N^{-1/2} + 5992.7 N^{-1} - 3665 N^{-3/2} \,. \tag{5}$$

The coefficients of Eq. (5) were determined with the use of the recommended values of T_{cr} for pure alkanes [6] with variation of the number of carbon atoms in the alkane molecule N from 5 to 18.

As a result of processing the experimental data on the velocity of sound, the parameters of Eqs. (2) and (3) were calculated and their values are presented in Table 2. The same table also gives the T_{cr} values calculated by (5). Equation (2) describes the input data on the velocity of sound at T = 298–433 K and p = 0.1–100 MPa for each composition of the mixture with an rms and a maximum deviation of 0.02 and 0.05%, respectively.

Input Data. To calculate the thermodynamic properties of the mixture at high pressures, it is necessary to have additional experimental information on the density ρ_0 and the isobaric heat capacity c_{p_0} at atmospheric pressure. Analysis of the literature data on ρ_0 and c_{p_0} has shown that there are only disconnected data for individual mixtures of alkanes in narrow temperature ranges. For the $C_{12} + C_{16}$ mixture, several works are known [7–10] in which measurements of ρ_0 and c_{p_0} were made. In [7], the density was measured at temperatures of 298–358 K, and in [8, 9] — at a temperature of 298.15 K. In [10], the excess isobaric heat capacity was investigated in the 293–328 K range of temperatures. The scarceness of data on ρ_0 and c_{p_0} incited us to conduct additional works on the joint study of the behavior of the aforesaid properties depending on the molar mass of pure homologs and their binary mixtures [11]. On the basis of the most reliable experimental data it was established that within the measurement error the dependences of the molar volume and the molar isobaric heat capacity on the molar mass of pure homologs in the series from C_6 to C_{16} and their binary mixtures are close to linear ones. This permitted determining by graph-analytic interpolation the deficient values of ρ_0 and c_{p_0} of the mixture for temperatures of 298–433 K. The thus-obtained values together with the available experimental data were used to find analytical expressions for the density and the heat capacity at atmospheric pressure:

$$\rho_0 = \sum_{i=0}^{3} a_i \, (T_{\mathrm{cr}} - T)^i \,, \tag{6}$$

$$c_{p_0} = \sum_{i=0}^{4} c_i T^i \,. \tag{7}$$

The values of the coefficients a_i and c_i calculated by the least-square technique are presented in Table 3.

TABLE 4. Thermodynamic Properties of the Binary Liquid Mixture *n*-dodecane+*n*-hexadecane (molar concentrations)

T, K	W, m/s	ρ, kg/m^3	c_p, kJ/(kg·K)	c_v, kJ/(kg·K)	$\alpha_p \cdot 10^3$, K^{-1}	$\beta_T \cdot 10^3$, MPa^{-1}
1	2	3	4	5	6	7
$x = 0.25$						
$p = 0.1$ MPa						
298.15	1326.7	765.0	2.211	1.852	0.904	0.887
313.15	1270.7	754.6	2.253	1.892	0.923	0.978
333.15	1198.7	740.6	2.314	1.950	0.950	1.115
353.15	1129.4	726.5	2.377	2.012	0.979	1.275
373.15	1062.4	712.2	2.444	2.077	1.013	1.464
393.15	997.4	697.6	2.513	2.145	1.050	1.688
413.15	934.4	682.8	2.587	2.218	1.093	1.957
433.15	873.3	667.8	2.669	2.299	1.141	2.280
$p = 20$ MPa						
298.15	1432.3	777.4	2.199	1.861	0.809	0.741
313.15	1381.6	768.0	2.240	1.900	0.818	0.804
333.15	1317.2	755.4	2.298	1.958	0.832	0.896
353.15	1256.0	742.9	2.359	2.019	0.845	0.997
373.15	1197.9	730.3	2.423	2.084	0.858	1.110
393.15	1142.5	717.8	2.489	2.151	0.873	1.235
413.15	1089.9	705.3	2.560	2.224	0.888	1.374
433.15	1039.9	692.8	2.637	2.303	0.904	1.529
$p = 40$ MPa						
313.15	1476.7	779.5	2.231	1.908	0.743	0.688
333.15	1417.3	768.0	2.288	1.965	0.750	0.755
353.15	1361.3	756.5	2.349	2.027	0.756	0.827
373.15	1308.4	745.1	2.412	2.091	0.761	0.904
393.15	1258.5	733.8	2.477	2.158	0.766	0.987
413.15	1211.4	722.6	2.546	2.230	0.772	1.077
433.15	1167.1	711.5	2.622	2.307	0.778	1.172
$p = 60$ MPa						
313.15	1560.3	789.6	2.225	1.915	0.686	0.604
333.15	1504.6	778.8	2.282	1.973	0.689	0.656
353.15	1452.3	768.1	2.343	2.034	0.691	0.711
373.15	1403.1	757.6	2.405	2.098	0.692	0.769
393.15	1356.8	747.2	2.470	2.165	0.693	0.829
413.15	1313.3	736.9	2.538	2.236	0.694	0.893
433.15	1272.5	726.7	2.613	2.312	0.696	0.960
$p = 80$ MPa						
313.15	1635.6	798.7	2.220	1.923	0.640	0.540
333.15	1582.8	788.5	2.278	1.980	0.641	0.583
353.15	1533.3	778.5	2.339	2.041	0.641	0.626
373.15	1486.8	768.5	2.401	2.105	0.640	0.671
393.15	1443.2	758.8	2.465	2.171	0.639	0.718
413.15	1402.2	749.2	2.533	2.241	0.637	0.767
433.15	1363.8	739.7	2.607	2.317	0.636	0.818
$p = 100$ MPa						
333.15	1653.9	797.3	2.275	1.986	0.602	0.525
353.15	1606.6	787.7	2.336	2.047	0.601	0.561
373.15	1562.3	778.3	2.398	2.111	0.599	0.598
393.15	1520.8	769.1	2.463	2.177	0.596	0.636
413.15	1481.8	760.0	2.530	2.247	0.593	0.675
433.15	1445.2	751.1	2.603	2.322	0.591	0.715
$x = 0.5$						
$p = 0.1$ MPa						
298.15	1312.7	759.4	2.209	1.844	0.923	0.916
313.15	1256.5	748.8	2.252	1.885	0.942	1.011
333.15	1184.2	734.7	2.314	1.944	0.970	1.155
353.15	1114.4	720.3	2.379	2.008	1.001	1.324

TABLE 4. Continued

1	2	3	4	5	6	7
373.15	1046.8	705.8	2.447	2.075	1.037	1.525
393.15	981.1	691.0	2.519	2.145	1.077	1.765
413.15	917.2	676.0	2.595	2.220	1.124	2.056
433.15	855.0	660.6	2.679	2.302	1.178	2.410
p = 20 MPA						
298.15	1420.3	772.1	2.196	1.852	0.823	0.761
313.15	1369.6	762.5	2.238	1.893	0.833	0.826
333.15	1305.0	749.8	2.297	1.952	0.846	0.922
353.15	1243.6	737.2	2.360	2.016	0.860	1.027
373.15	1185.2	724.5	2.426	2.082	0.874	1.145
393.15	1129.5	711.8	2.494	2.152	0.889	1.276
413.15	1076.4	699.2	2.566	2.226	0.904	1.423
433.15	1025.9	686.5	2.645	2.307	0.922	1.587
p = 40 MPa						
313.15	1466.0	774.2	2.229	1.901	0.756	0.705
333.15	1406.5	762.6	2.288	1.960	0.762	0.774
353.15	1350.4	751.0	2.350	2.023	0.767	0.848
373.15	1297.4	739.5	2.414	2.090	0.772	0.928
393.15	1247.3	728.2	2.481	2.159	0.777	1.014
413.15	1200.0	716.9	2.551	2.232	0.783	1.107
433.15	1155.4	705.7	2.629	2.312	0.789	1.207
p = 60 MPa						
313.15	1550.7	784.5	2.223	1.909	0.697	0.617
333.15	1494.9	773.6	2.281	1.968	0.699	0.671
353.15	1442.5	762.9	2.343	2.031	0.701	0.727
373.15	1393.2	752.3	2.407	2.097	0.701	0.786
393.15	1346.8	741.8	2.474	2.166	0.702	0.849
413.15	1303.1	731.4	2.543	2.239	0.702	0.915
433.15	1262.1	721.2	2.620	2.317	0.704	0.984
p = 80 MPa						
313.15	1626.8	793.7	2.218	1.916	0.650	0.551
333.15	1573.9	783.5	2.277	1.975	0.650	0.594
353.15	1524.3	773.3	2.339	2.038	0.649	0.639
373.15	1477.8	763.4	2.403	2.104	0.648	0.685
393.15	1434.0	753.6	2.469	2.173	0.646	0.733
413.15	1392.9	743.9	2.539	2.245	0.644	0.783
433.15	1354.4	734.4	2.614	2.323	0.642	0.835
p = 100 MPa						
333.15	1645.6	792.3	2.274	1.981	0.610	0.535
353.15	1598.3	782.7	2.337	2.045	0.608	0.572
373.15	1553.9	773.3	2.401	2.110	0.605	0.609
393.15	1512.3	764.0	2.467	2.179	0.602	0.648
413.15	1473.1	754.9	2.536	2.251	0.598	0.688
433.15	1436.4	745.9	2.611	2.328	0.596	0.729
x = 0.75						
p = 0.1 MPa						
298.15	1297.0	752.9	2.207	1.835	0.944	0.949
313.15	1240.2	742.2	2.251	1.878	0.964	1.050
333.15	1167.0	727.8	2.315	1.940	0.994	1.204
353.15	1096.3	713.3	2.382	2.005	1.028	1.386
373.15	1027.7	698.5	2.453	2.074	1.066	1.603
393.15	961.0	683.5	2.527	2.146	1.111	1.865
413.15	896.1	668.1	2.606	2.224	1.162	2.184
433.15	833.0	652.4	2.693	2.308	1.221	2.577
p = 20 MPa						
298.15	1406.3	765.9	2.194	1.844	0.839	0.785

TABLE 4. End

1	2	3	4	5	6	7
313.15	1355.2	756.3	2.236	1.887	0.849	0.853
333.15	1290.2	743.4	2.298	1.948	0.862	0.953
353.15	1228.3	730.6	2.362	2.013	0.877	1.064
373.15	1169.5	717.8	2.429	2.082	0.891	1.189
393.15	1113.4	705.0	2.499	2.153	0.907	1.328
413.15	1060.1	692.2	2.574	2.230	0.925	1.484
433.15	1009.5	679.4	2.655	2.313	0.943	1.658
p = 40 MPa						
313.15	1452.9	768.2	2.227	1.895	0.768	0.725
333.15	1393.2	756.5	2.288	1.956	0.774	0.796
353.15	1336.8	744.8	2.351	2.021	0.780	0.874
373.15	1283.7	733.3	2.417	2.090	0.785	0.957
393.15	1233.4	721.8	2.486	2.161	0.790	1.048
413.15	1186.1	710.4	2.558	2.236	0.796	1.145
433.15	1141.6	699.2	2.638	2.318	0.803	1.249
p = 60 MPa						
313.15	1538.6	778.7	2.221	1.903	0.708	0.633
333.15	1482.6	767.7	2.281	1.964	0.709	0.688
353.15	1430.1	756.9	2.345	2.029	0.710	0.746
373.15	1380.8	746.2	2.410	2.097	0.711	0.808
393.15	1334.3	735.7	2.478	2.168	0.712	0.873
413.15	1290.7	725.3	2.550	2.243	0.713	0.941
433.15	1249.8	715.0	2.628	2.323	0.714	1.013
p = 80 MPa						
313.15	1615.4	788.1	2.217	1.911	0.659	0.564
333.15	1562.4	777.7	2.277	1.972	0.659	0.608
353.15	1512.8	767.6	2.341	2.037	0.658	0.654
373.15	1466.2	757.5	2.406	2.104	0.656	0.702
393.15	1422.5	747.7	2.474	2.175	0.654	0.752
413.15	1381.5	738.0	2.545	2.249	0.652	0.803
433.15	1343.1	728.4	2.622	2.328	0.651	0.857
p = 100 MPa						
333.15	1634.8	786.8	2.275	1.979	0.618	0.547
353.15	1587.5	777.1	2.338	2.043	0.615	0.584
373.15	1543.1	767.6	2.403	2.111	0.612	0.623
393.15	1501.5	758.3	2.471	2.181	0.608	0.663
413.15	1462.5	749.2	2.542	2.255	0.605	0.704
433.15	1426.0	740.2	2.618	2.333	0.603	0.746

According to our estimates, the error in the input data on ρ_0 and W used to calculate the thermodynamic properties does not exceed 0.1%, and on c_{p_0} — 0.5%.

Computational Procedure. To calculate the thermodynamic properties of the liquid mixture $C_{12} + C_{16}$ on the basis of the data on the velocity of sound, we used an iterative stepwise procedure.

The computational procedure is based on the known thermodynamic equations

$$\rho = \rho_0 + \int_{p_0}^{p} \frac{1}{W^2}\, dp + T \int_{p_0}^{p} \frac{\alpha_p^2}{c_p}\, dp\,, \tag{8}$$

$$c_p = c_{p_0} - \frac{T}{\rho} \int_{p_0}^{p} \left[\alpha_p^2 + \left(\frac{\partial \alpha_p}{\partial T} \right)_p \right] dp\,, \tag{9}$$

$$\beta_T = \frac{1}{\rho} \left(\frac{1}{W^2} + \frac{T\alpha_p^2}{c_p} \right), \tag{10}$$

TABLE 5. Parameters of Equations (12) and (13)

Parameter	x				
	0 [2]	0.25	0.5	0.75	1 [12]
A	0.08744	0.08626	0.08633	0.086446	0.0881
b_0	–96.3	–92.12	–92.9	–90.81	–77.51
b_1	82.37	78.625	80.065	78.339	63.67
b_2	–0.07	0.673	0.4214	1.025	5.639

$$c_v = \frac{c_p}{1 + \dfrac{T\alpha_p^2 W^2}{c_p}}, \tag{11}$$

in which $\alpha_p = -\dfrac{1}{\rho}\left(\dfrac{\partial\rho}{\partial T}\right)_p$.

The calculation was performed for isotherms by the iterative stepwise procedure with a small pressure step (increment) $\Delta p = 0.2$ MPa. To calculate ρ, in Eq. (8) the second term $\int_{p_0}^{p} W^{-2}dp$ was integrated analytically with the use of (2), and the third term was integrated numerically. To calculate c_p by Eq. (9), numerical integration was used. The values of α_p and $\left(\dfrac{\partial\alpha_p}{\partial T}\right)_p$ were determined by differentiating a polynomial similar to (6) by which the ρ value was approximated at each pressure step. Then, on the basis of obtained values of ρ, c_p, α_p, and W, the values of β_T and c_v were calculated by formulas (10) and (11). The computational procedure is described in detail in [2]. The results of the calculation are presented in Table 4. According to our estimates, the errors in the calculated values of the thermodynamic properties are the largest at a pressure of 100 MPa and a temperature of 433.15 K. At these parameters they do not exceed 0.15% for ρ, 1% for c_p, 1.5% for c_v, 1.7% for α_p, and 1% for β_T.

Results and Discussion. In the case of the $C_{12} + C_{16}$ mixture, comparison of results of the calculation of the thermodynamic properties with direct-measurement data only on the density is possible. In [8, 9], density measurements were made at atmospheric pressure and a temperature of 298.15 K in the range of molar concentrations 0.2–0.8 and 0–1 with errors of ±0.5 kg/m^3 and ±0.02 kg/m^3, respectively. In [7], an equimolar mixture was investigated, respectively, at temperatures of 298.15, 318.15, 338.15, and 358.15 K and pressures of 0.1–55.7, 0.1–124.2, 0.1–219.8, and 0.1–331.3 MPa with an error of 0.06%. The comparison made has shown that at atmospheric pressure the data of [8, 9] agree with the results of the calculation within the limits of ±0.02–0.04%, and the values obtained in [7] are 0.05% lower. At high pressures the measurement data of [7] are lower at 298.15 and 318.15 K by 0.06% on average, and at 338.18 and 358.15 K — by 0.13%, which is within the computational error. Thus, the comparison shows a good agreement between the experimental and calculated density values.

Generalizing Relations. The calculated values of the density were generalized by the Tate equation

$$\rho = \frac{\rho_0}{1 - A\ln\left(\dfrac{B+p}{B+p_0}\right)}, \tag{12}$$

$$B = b_0 + b_1\left(\frac{T_\mathrm{cr}}{T}\right) + b_2\left(\frac{T_\mathrm{cr}}{T}\right)^2. \tag{13}$$

The parameters of Eqs. (12) and (13) for three compositions of the mixture are given in Table 5. The same table also presents their values for pure alkanes C_{12} and C_{16} [2, 12]. Equation (12) describes well the initial values of the density in the investigated range of parameters T = 298–433 K and p = 0.1–100 MPa. The standard and the maximum deviation of the density values calculated by (12) from the initial values for all mixtures does not exceed, respectively, 0.01 and 0.05%. It should be noted that (12) has good extrapolation possibilities for the pressure. It reproduces with a fair accuracy (0.1–0.2%) the data on the density [7] at temperatures of 298.15–358.15 K and pressures of up to 331.3 MPa.

The Tate equation was used by us to describe the binary mixtures of alkanes. The concentration dependences of the density ρ_0 and the parameter B were sought in the form

$$\rho_0 = \frac{xM_1 + (1-x)\,M_2}{V_0^{\mathrm{E}} + \dfrac{xM_1}{\rho_{01}} + \dfrac{(1-x)\,M_2}{\rho_{02}}}\,, \tag{14}$$

$$B = xB_1 + (1-x)\,B_2 + Cx\,(1-x)\,(B_1 - B_2)^2\,. \tag{15}$$

The excess molar volume at atmospheric pressure V_0^{E} determined by the data on the density of the mixture and pure components was approximated by the Redlich–Kister equation

$$V_0^{\mathrm{E}} = x\,(1-x)\,[D_0 + D_1\,(2x-1)]\,. \tag{16}$$

The temperature functions D_0 and D_1 have the form

$$D_0 = 1.903\cdot10^{-6} - 7.09\cdot10^{-7}\left(\frac{T}{100}\right), \tag{17}$$

$$D_1 = 6.543\cdot10^{-7} - 2.88\cdot10^{-7}\left(\frac{T}{100}\right). \tag{18}$$

For the mixture, A = 0.087411 and C = 0.02425.

The values of ρ_{01}, ρ_{02} and B_1, B_2 were calculated by (6) and (13) with the coefficients given, respectively, in Tables 3 and 5. Equation (12) jointly with (14)–(16) can be recommended for practical calculations of the $C_{12} + C_{16}$ mixture density at temperatures of 298–433 K, pressures of 0.1–100 MPa, and molar concentrations of 0–1. It describes the density values presented in Table 4 and the data of [7] with a deviation not exceeding, on average, 0.05 and 0.1%, respectively.

Of particular interest was the estimation of the applicability of the Bransted and Koefoed principle of congruence (coincidence) [13] for the region of high parameters. A mixture of two alkanes with the numbers of carbon atoms N_1 and N_2 is congruent to a pure alkane with the number of carbon atoms N determined by (4). It is customary to call such mixtures pseudoalkanes or equivalent alkanes. However, in the literature there is no generally accepted terminology on this point. In accordance with the principle of congruence, such mixtures and their corresponding pure alkanes should have coinciding numerical values of a particular property at given temperatures and pressures. But if mixtures of homologs have noninteger values of N, then their properties lie in the same series (on a single curve) with the properties of pure homologs at given parameters. It is easy to determine that the mixtures $0.75C_{12} + 0.25C_{16}$, $0.5C_{12} + 0.5C_{16}$, and $0.25C_{12} + 0.75C_{16}$ are congruent to the pure alkanes C_{13}, C_{14}, and C_{15}, respectively. The performed comparison of the experimental values of W and the calculated values of ρ, c_p, c_v, α_p, and β_T for the analyzed mixture of the three compositions with the values of the properties for C_{13} [14], C_{14} [15], and C_{15} [16] has shown that at T = 298–433 K and p = 0.1–100 MPa a good agreement is observed. The discrepancies practically never fall outside the limits of the estimated computational error of the above properties in the present work. The only exception is α_p, for which the discrepancy at temperatures of 393–433 K and pressures of 0.1–100 MPa are within the limits of

1.5–3.6%. Thus, the calculations and estimations made point to the possibility of using the principle of congruence also in the region of high parameters.

Conclusions. We have presented the results of an experimental investigation of the velocity of sound in a binary liquid mixture *n*-dodecane+*n*-hexadecane of three compositions in the following range of parameters: T = 298.15–433.15 K; p = 0.1–100.1 MPa. Analysis of the concentration dependence of the velocity of sound for the investigated mixture has been carried out. It has been shown that for the *n*-dodecane+*n*-hexadecane mixture the molar-additive rule is not observed. An algorithm and a program for calculating the thermodynamic properties of liquid mixtures on the basis of data on the velocity of sound have been proposed and realized. As a result of the calculations, for the first time a table of thermodynamic properties of the mixture *n*-dodecane+*n*-hexadecane at temperatures of 298–433 K, pressures of 0.1–100 MPa, and a molar concentration of *n*-dodecane of 0.25, 0.50, and 0.75 has been obtained. The coefficients of the Tate equations for individual compositions and for the mixture on the whole in the above range of state parameters have been determined.

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NOTATION

A, constant of the Tate equation (12); a_i, approximation coefficient of Eq. (6); B, temperature-dependent parameter of the Tate equation (12), MPa; B_1, B_2, parameters depending on the temperature of dodecane and hexadecane, respectively; b_0, b_1, b_2, coefficients of Eq. (13); C, constant of Eq. (15); c_i, approximation constants of Eq. (7); c_{p_0}, isobaric heat capacity at atmospheric pressure, kJ/(kg·K); c_p, c_v, isobaric and isochoric heat capacities, respectively, kJ/(kg·K); D_0, D_1, temperature functions of Eq. (16); E_0, E_1, E_2, E_3, constants of Eq. (2); E_4, temperature function of Eq. (2); e_0, e_1, approximation coefficients of Eq. (3); k, exponent of Eq. (3); M_1, M_2, molar masses of dodecane and hexadecane, respectively, kg/mol; N, average number of carbon atoms of the components in the mixture; N_1, N_2, numbers of carbon atoms in molecules of the first and second components, respectively; p, pressure, MPa; p_0, atmospheric pressure, MPa; Δp, pressure step (increment), MPa; T, temperature, K; T_{cr}, critical temperature, K; V_0^{E}, excess molar volume, m^3/mol; W_1, W_2, W, velocities of sound in the pure components and in the mixture, respectively, m/s; x, molar concentration of dodecane; x_1, x_2, molar concentrations of the first and second components, respectively; α_p, isobaric expansion coefficient, K^{-1}; $(\partial\alpha_p/\partial T)_p$, derivative of the isobaric expansion coefficient, K^{-2}; β_T, isothermal compressibility, MPa^{-1}; ρ, density, kg/m^3; ρ_0, density at atmospheric pressure, kg/m^3; ρ_{01}, ρ_{02}, densities at atmospheric pressure of dodecane and hexadecane, respectively, kg/m^3. Subscripts and superscripts: E, excess; i, coefficient number; cr, critical state; values of p, v, T, at constant pressure, volume, and temperature, respectively; 0, for equation coefficients means the coefficient number, and for p, V^{E}, ρ, and c_p — atmospheric pressure.

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