Temperature Dependence of the Speed of Sound, Densities, and Isentropic Compressibilities of Hexane + Hexadecane in the Range of (293.15 to 373.15) K

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The speed of sound u and density ρ for the binary mixture hexane + hexadecane has been measured as a function of composition and temperature along the saturation line between 293.15 K and 373.15 K. The speed of sound was measured by a pulse-phase echo ultrasonic device at a frequency of (1 to 5) MHz with an uncertainty of ±0.1%. The density was measured by an Ostwald−Sprengel-type pycnometer with an uncertainty of $\pm 3 \times 10^{-5}$ g·cm^{-3}. The experimental results were used to calculate deviations of the speed of sound Δu, excess molar volume V^E, and isentropic compressibility k_S. The values Δu and V^E were fitted by the Redlich−Kister equation.

Introduction

Experimental data of *n*-alkane binary liquid mixtures at room temperatures are widely covered in the literature.[1−3] However, information about the composition and temperature dependence of the thermophysical properties of *n*-alkane binary liquid systems is rather limited. The aim of the present work is to report data for the speed of sound u and density ρ for the binary mixture of hexane + hexadecane over the whole range of composition, at the saturation line, and in the temperature range of (293.15 to 373.15) K. In this work, we report the calculated values of isentropic compressibilities k_S, excess molar volumes V^E, and changes in the speed of sound for these mixtures. The excess molar volumes were compared with those measured by Marsh et al.[4] at 313. 15 K and Dymond et al.[5] at 298.15 K. This paper is part of a program in our laboratory of molecular acoustics aimed at providing reliable acoustic data of binary liquid mixtures.

Experimental Section

Materials. Hexane and hexadecane (mole fraction >0.99) were supplied from Sigma-Aldrich Ltd. All chemicals were partially degassed and dried over Fluka 0.4 nm molecular sieves. The purity of the products was checked by gas chromatography (GC). The mole fractions of hexane and hexadecane were 99.7% and 99.5%, respectively. The mixtures were prepared by mass with a precision of $\pm 5 \times 10^{-5}$ g. The uncertainty in the mole fraction is less than 1×10^{-4}. All molar quantities are based on the IUPAC relative atomic mass table (IUPAC, 1986).[6]

Measurements. The ultrasonic speed was measured along the saturation line with our pulse-phase echo ultrasonic device, with a precision of ±1 m·s^{-1}. The details of the method and technique used to determine the speed of sound have been described previously.[7] The speed of sound was measured at a frequency of (1 to 5) MHz. Dispersion was not observed. The speed-of-sound measuring cell was thermostated with a temperature stability of ±0.01 K. The temperature was measured with a platinum resistance thermometer with an uncertainty of ±0.01 K. Densities were measured with an Ostwald−Sprengel-type pycnometer, with a capacity of approximately 50 cm^3. The uncertainty in the density measurements was estimated to be $\pm 3 \times 10^{-5}$ g·cm^{-3}. Experimental values of the density and speed of sound for hexane and hexadecane were compared with those found in the literature, and they were found to be in fairly good agreement (with the exception of speed-of-sound data for hexane presented in ref 8), as shown in Table 1. The experimental results of the speed of sound u and density ρ in the liquid phase for hexane and hexadecane are listed in Table 2. The values of the speed of sound from (293.15 to 373.15) K and density from (293.15 to

Table 1. Comparison of Experimental Densities ρ and Speed of Sound u with Literature Data for Pure Liquids at Different Temperatures

		ρ/kg·m^{-3}		u/m·s^{-1}	
liquid	T/K	this work	lit	this work	lit
hexane	293.15	659.44	659.40[9]	1098	1099.8[16]
	298.15	654.93	654.89[10]	1076	1078.1[17]
			654.8[11]		1085.68[8]
			654.98[12]		
			655.08[13]		
	303.15	650.36	650.2[11]	1054	1052.2[17]
					1054.6[16]
	308.15	645.74	645.86[13]	1032	
	323.15	631.61	631.5[11]	966	971.42[8]
			631.82[13]		964.7[16]
	333.15	621.95	621.9[14]	921	920.7[17]
			621.8[11]		920.6[16]
hexadecane	298.15	769.97	769.94[15]	1338	1339.22[8]
			770.2[5]		
			770.0[11]		
	303.15	766.55	766.5[11]	1319	1320.0[17]
	323.15	752.79	753.0[5]	1247	1248.11[8]
	333.15	745.86	745.9[11]	1211	1211.4[17]
			746.1[15]		
	348.15	735.42	735.8[5]	1159	1160.59[8]
	373.15	717.88	717.9[11]	1073	1076.2[17]
			718.6[5]		1074.99[8]

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Table 2. Speed of Sound u and Density ρ of Hexane and Hexadecane from (293.15 to 373.15) K

T/K	u/m·s^{-1}	ρ/kg·m^{-3}	T/K	u/m·s^{-1}	ρ/kg·m^{-3}
		Hexane			
293.15	1098	659.44	338.15	900	
298.15	1076	654.93	343.15	878	
303.15	1054	650.36	348.15	856	
308.15	1032	645.74	353.15	834	
313.15	1010	641.08	358.15	812	
318.15	988	636.37	363.15	790	
323.15	966	631.61	368.15	768	
328.15	944	626.81	373.15	747	
333.15	921	621.95			
		Hexadecane			
293.15	1357	773.38	338.15	1193	742.39
298.15	1338	769.97	343.15	1176	738.91
303.15	1312	766.55	348.15	1158	735.42
308.15	1301	763.12	353.15	1141	731.93
313.15	1283	759.68	358.15	1124	728.43
318.15	1265	756.24	363.15	1107	724.92
323.15	1246	752.79	368.15	1090	721.4
328.15	1228	749.33	373.15	1074	717.88
333.15	1211	745.86			

Table 3. Speed of Sound u of Hexane (1) + Hexadecane (2) from (293.15 to 373.15) K

	x_1								
T/K	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
					u/m·s^{-1}				
293.15	1341	1327	1314	1297	1277	1254	1228	1196	1151
298.15	1322	1308	1295	1277	1257	1234	1207	1175	1129
303.15	1304	1289	1275	1258	1237	1215	1187	1154	1108
308.15	1285	1270	1256	1238	1217	1195	1167	1133	1086
313.15	1266	1251	1237	1219	1198	1175	1146	1112	1065
318.15	1248	1232	1219	1200	1178	1156	1126	1091	1044
323.15	1230	1214	1200	1181	1159	1136	1107	1071	1023
328.15	1211	1196	1182	1163	1140	1117	1087	1050	1002
333.15	1193	1177	1163	1144	1122	1098	1067	1030	981
338.15	1176	1160	1145	1126	1103	1079	1048	1010	960
343.15	1158	1142	1127	1108	1084	1060	1029	990	939
348.15	1140	1124	1109	1089	1066	1042	1010	971	918
353.15	1123	1106	1092	1072	1048	1023	991	951	898
358.15	1106	1089	1074	1054	1030	1005	972	932	877
363.15	1088	1071	1057	1036	1012	986	953	912	857
368.15	1072	1054	1039	1019	995	968	935	893	837
373.15	1055	1037	1022	1002	977	950	916	874	816

333.15) K of the binary mixture hexane (1) + hexadecane (2) are given in Tables 3 and 4, respectively.

Results and Discussion

The speed of sound, u, values are fitted by the method of least squares using the polynomial

$$u = A_0 + A_1T + A_2T^2 \tag{1}$$

Here, T is the absolute temperature and A_0, A_1, and A_2 are adjustable parameters. The parameters are presented in

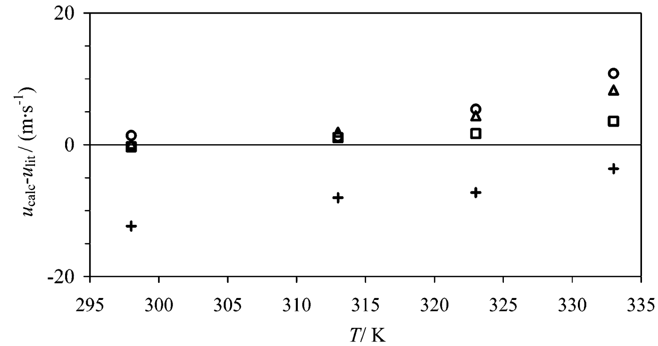

Figure 1. Deviation of the speed of sound u for hexane (1) + hexadecane (2) for the data of Ye at al.[18] from eq 1: +, x_1 = 0.2; □, x_1 = 0.4; ○, x_1 = 0.6; △, x_1 = 0.8.

Table 5 along with the standard deviation σ defined by

$$\sigma = \left[\left\{\sum_{i=1}^{n}\frac{(u_{\text{obsd}} - u_{\text{calcd}})^2}{n - p}\right\}\right]^{1/2} \tag{2}$$

where u_{obsd} and u_{calcd} are the observed and calculated quantities as defined earlier, n is the total number of experimental points, and p is the number of parameters.

We have compared our results for the speed of sound of the researched mixture at 298.35 K, 313.15 K, 323.15 K, and 333.15 K with the data reported by Ye et al.[18] As shown in Figure 1, it was found that their results at 298.35 K typically deviated by 0.5 m·s^{-1} from the values calculated with eq 1 with the exception of the value −12.3 m·s^{-1} at x_1 = 0.2. By analogy to the data at 298.35 K, a typically deviation of the data of Ye at al. from eq 1 is 1 m·s^{-1}, except for the value −8 m·s^{-1} at x_1 = 0.2. However, an increase of the temperature difference between our data and the data of Ye et al. increases significantly.

The excess molar volume V^E and deviations in the speed of sound Δu of the mixtures have been calculated using the following equations

$$V^E = V - (x_1V_1 + x_2V_2) \tag{3}$$

$$\Delta u = u - (x_1u_1 + x_2u_2) \tag{4}$$

where x_1 and x_2 are the mole fractions; u_1, u_2, and u are the speeds of sound of pure components and mixture; and V_1, V_2, and V are the molar volumes of the pure components and mixture, respectively. The molar volume V is defined by the relation

$$V = \frac{x_1M_1 + x_2M_2}{\rho}$$

where M_1 and M_2 are the molar masses of the pure

Table 4. Density ρ of Hexane (1) + Hexadecane (2) from (293.15 to 333.15) K

	x_1								
T/K	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
					ρ/kg·m^{-3}				
293.15	768.10	762.36	756.02	748.67	740.14	729.79	717.46	702.30	683.23
298.15	764.70	758.88	752.56	745.03	736.52	726.08	713.68	698.40	679.04
303.15	761.25	755.40	749.09	741.49	732.90	722.32	709.86	694.47	674.80
308.15	757.78	751.90	745.61	737.93	729.25	718.63	706.03	690.50	670.53
313.15	754.31	748.41	741.92	734.37	725.59	714.88	702.18	686.49	666.22
318.15	750.84	744.91	738.42	730.80	721.92	711.12	698.30	682.45	661.87
323.15	747.36	741.40	734.92	727.21	718.23	707.34	694.38	678.36	657.47
328.15	743.88	737.89	731.41	723.62	714.52	703.55	690.44	674.25	653.04
333.15	740.37	734.36	727.88	720.01	710.80	699.74	686.47	670.09	648.56

Table 5. Values of the Parameters of Equation 1 and Standard Deviation for Hexane (1) + Hexadecane (2) from (293.15 to 373.15) K

x_1	A_1	A_2	A_3	σ/m·s^{-1}
0	2660.3	−5.1612	2.435×10^{-3}	0.08
0.1	2698.5	−5.4528	2.8065×10^{-3}	0.23
0.2	2695.2	−5.4943	2.8168×10^{-3}	0.17
0.3	2718.2	−5.6897	3.0671×10^{-3}	0.09
0.4	2718.4	−5.7649	3.1187×10^{-3}	0.22
0.5	2749.8	−6.0346	3.4422×10^{-3}	0.09
0.6	2665.1	−5.6053	2.7049×10^{-3}	0.23
0.7	2706.8	−5.9471	3.0789×10^{-3}	0.20
0.8	2700.4	−6.0088	2.9886×10^{-3}	0.11
0.9	2575.8	−5.3921	1.8132×10^{-3}	0.37
1	2437.9	−4.7075	4.6904×10^{-3}	0.43

Table 6. Values of Δu for the Binary Mixture Hexane (1) + Hexadecane (2) from (293.15 to 373.15) K

	x_1								
T/K	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	Δu/m·s^{-1}								
293.15	11	22	35	43	49	53	52	46	27
298.15	11	22	35	44	50	53	53	46	27
303.15	11	22	35	44	50	54	53	46	27
308.15	11	22	36	45	51	55	54	47	28
313.15	11	23	36	45	51	56	55	47	28
318.15	11	23	37	46	52	57	56	48	29
323.15	11	23	38	47	53	58	57	49	29
328.15	11	24	38	48	54	59	58	50	29
333.15	11	24	39	49	55	61	59	51	30
338.15	12	25	40	50	56	62	60	52	31
343.15	12	25	41	51	58	63	62	53	32
348.15	12	26	41	52	59	65	63	54	32
353.15	12	26	42	53	60	66	64	56	33
358.15	13	27	43	55	62	68	66	57	34
363.15	13	28	44	56	64	69	68	59	35
368.15	14	29	46	57	65	71	70	61	36
373.15	14	29	47	59	67	73	72	62	37

components and ρ is the density of the mixture. Experimental values Δu and V^E at various temperatures are reported in Tables 6 and 7. Uncertainty in the changes Δu and V^E were estimated to be better than ± 2 m·s^{-1} and ± 0.02 cm^3·mol, respectively. The excess molar volume V^E and the change in the speed of sound upon mixing Δu were fitted by a Redlich−Kister-type equation[19]

$$\Delta u/\text{m·s}^{-1} \text{ or } V^E/\text{cm}^3\text{·mol}^{-1} = x_1 x_2 \sum_{j=0}^{k} B_j (2x_2 - 1)^j \quad (5)$$

The coefficient B_j in eq 5 was estimated by the least-squares fitting method. The values of parameters B_j and standard deviation $\sigma(\Delta u)$ are given in Table 8 at temperatures from (293.15 to 373.15) K. $\sigma(\Delta u)$ values were calculated for a ratio of the type seen in eq 2. As can be seen from Figure 2, our composition dependence of V^E at 313.15 K is in reasonably good agreement with data presented by Marsh at al.[4] The experimental results of the excess molar volume V^E and deviations of the speed of sound Δu for hexane + hexadecane at various temperatures are plotted as a function of composition in Figures 3 and 4. It is interesting that extreme values of deviations of the speed of sound and excess molar volume are at $x_1 \approx$ 0.6.

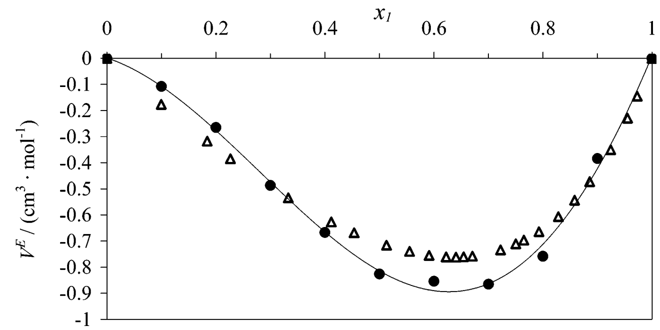

Figure 2. Excess molar volumes V^E for hexane (1) + hexadecane (2) at 313.15 K: ●, this work; △, ref 4.

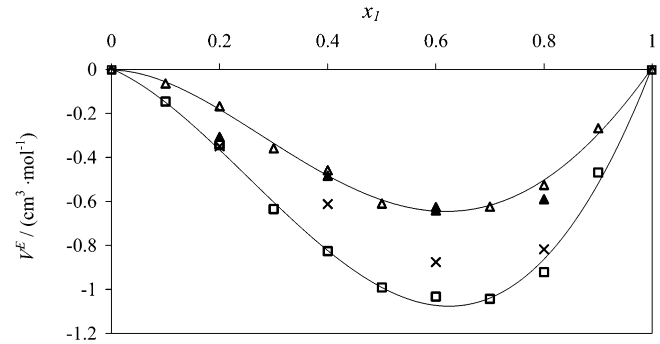

Figure 3. Excess molar volumes V^E for hexane (1) + hexadecane (2): △, 298.15 K (this work); □, 323.15 K (this work); ▲, 298.15 K (ref 5); ×, 323.15 (ref 5).

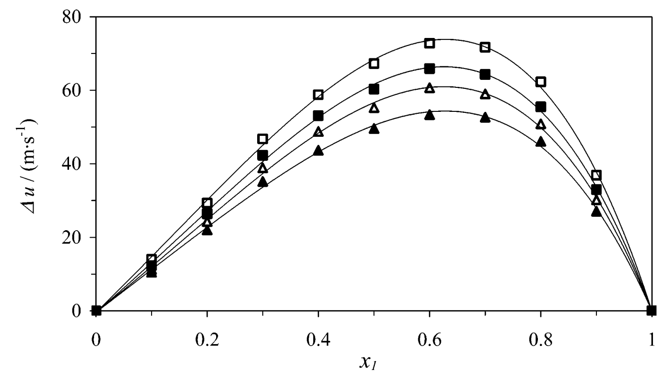

Figure 4. Deviation of the speed of sound for hexane (1) + hexadecane (2): ▲, 298.15 K; △, 333.15 K; ■, 353.15 K; □, 373.15 K.

Table 7. Excess Molar Volumes V^E of the Binary Mixture Hexane (1) + Hexadecane (2) from (293.15 to 333.15) K

	x_1								
T/K	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	V^E/cm^3·mol								
293.15	−0.037	−0.143	−0.303	−0.432	−0.550	−0.563	−0.552	−0.454	−0.232
298.15	−0.065	−0.167	−0.359	−0.459	−0.610	−0.626	−0.624	−0.525	−0.267
303.15	−0.079	−0.197	−0.420	−0.524	−0.681	−0.685	−0.698	−0.602	−0.303
308.15	−0.091	−0.226	−0.486	−0.592	−0.751	−0.774	−0.780	−0.680	−0.343
313.15	−0.108	−0.265	−0.487	−0.667	−0.827	−0.855	−0.866	−0.759	−0.384
318.15	−0.127	−0.303	−0.557	−0.746	−0.907	−0.942	−0.954	−0.841	−0.427
323.15	−0.146	−0.344	−0.635	−0.827	−0.991	−1.034	−1.043	−0.923	−0.469
328.15	−0.171	−0.392	−0.717	−0.916	−1.078	−1.133	−1.137	−1.010	−0.515
333.15	−0.190	−0.439	−0.801	−1.009	−1.173	−1.238	−1.237	−1.099	−0.562

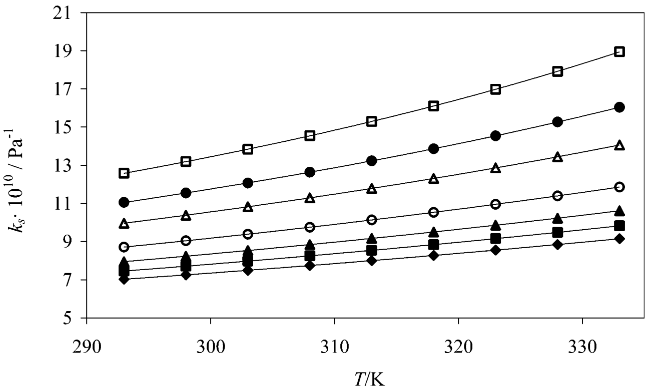

Figure 5. Isentropic compressibility k_S as a function of temperature for hexane (1) + hexadecane (2) from (293.15 to 333.15) K: ◆, $x_1 = 0$; ■, $x_1 = 0.2$; ▲, $x_1 = 0.4$; ○, $x_1 = 0.6$; △, $x_1 = 0.8$; ●, $x_1 = 0.9$; □, $x_1 = 1$.

Table 8. Parameters B_j of Equation 5 and Standard Deviation σ

T/K	B_0	B_1	B_2	B_3	σ
		Δu			
293.15	200.235	104.215	25.895	29.333	2.43
298.15	201.909	105.178	24.134	28.406	2.39
303.15	204.246	108.376	21.250	22.630	2.14
308.15	207.034	109.394	20.150	24.895	2.19
313.15	209.914	110.167	20.850	24.697	2.20
318.15	213.480	113.516	20.603	23.352	2.25
323.15	217.297	115.480	19.292	24.208	2.26
328.15	221.383	117.850	18.332	23.989	2.34
333.15	226.677	122.306	18.512	23.040	2.31
338.15	230.547	123.630	19.883	23.769	2.43
343.15	236.029	127.646	19.706	23.614	2.38
348.15	241.189	130.857	19.436	23.373	2.44
353.15	246.625	133.010	21.080	27.096	2.41
358.15	253.173	137.121	23.303	28.179	2.43
363.15	259.297	141.694	23.999	27.103	2.52
368.15	266.378	145.889	26.900	28.165	2.65
373.15	273.467	150.256	29.136	28.017	2.71
		V^E			
293.15	−2.158	−1.531	0.911	0.997	0.032
298.15	−2.374	−1.781	0.665	0.339	0.057
303.15	−2.653	−1.828	0.562	0.055	0.077
308.15	−2.972	−1.977	0.532	−0.076	0.083
313.15	−3.296	−2.149	0.268	−0.319	0.110
318.15	−3.606	−2.483	0.422	0.127	0.072
323.15	−3.968	−2.575	0.375	−0.040	0.081
328.15	−4.351	−2.670	0.292	−0.185	0.096
333.15	−4.763	−2.774	0.281	−0.379	0.108

Isentropic compressibilities k_S of the binary mixtures were calculated from the Laplace equation

$$k_S = \frac{1}{\rho u^2} \tag{6}$$

where u is the sound velocity and ρ is the density. The values of isentropic compressibility k_S for hexane + hexadecane as a functions of temperature from (293.15 to 333.15) K are plotted in Figure 5. The uncertainty in the calculated values of k_S was (0.1 to 0.2)%.

Literature Cited

(1) Cooper, E. F.; Asfour, A.-F. A. Densities and Kinematic Viscosities of Some C_6-C_{16} *n*-Alkane Binary Liquid Systems at 293.15 K. *J. Chem. Eng. Data* **1991**, *36*, 285−288.

(2) Garcia Sanchez, M.; Rey Losada, C. Excess Volumes of *n*-Hexane + *n*-Undecane between 288.15 and 308.15 K. *J. Chem. Eng. Data* **1991**, *36*, 75−77.

(3) Sims, M. J.; Winnick, J. Excess Volumes of Binary Liquid Mixtures of *n*-Alkanes. *J. Chem. Eng. Data* **1969**, *14*, 164−166.

(4) Marsh, K. N.; Organ, P. P. Excess Molar Enthalpies and Excess Volumes for Three- and Four-component *n*-Alkane Mixtures Simulating (*n*-Hexane + *n*-Hexadecane). *J. Chem. Thermodyn.* **1985**, *17*, 835−841.

(5) Dymond, J. H.; Young, K. J.; Isdale J. D. P, ρ, T Beheviour for *n*-Hexane + *n*-Hexadecane in the Range 298 to 373 K and 0.1 to 500 MPa. *J. Chem. Thermodyn.* **1979**, *11*, 887−895.

(6) IUPAC Commission on Atomic Weights and Isotopic Abundances, 1985. *Pure Appl. Chem.* **1986**, *58*, 1677−1692.

(7) Bolotnikov, M. F.; Neruchev, Yu. A. Speed of Sound of Hexane + 1-Chlorohexane, Hexane + 1-Iodohexane, and 1-Chlorohexane + 1-Iodohexane at Saturation Condition. *J. Chem. Eng. Data* **2003**, *48*, 411−415.

(8) Ball, S. J.; Trusler, J. P. M. Speed of Sound of *n*-Hexane and *n*-Hexadecane at Temperatures Between 298 and 373 K and Pressures up to 100 MPa. *Int. J. Thermophys.* **2001**, *22*, 427−443.

(9) Nath, J. Speeds of Sound in and Isentropic Compressibilities of (*n*-Butanol + *n*-Pentane, or *n*-Hexane, or *n*-Heptane, or 2,2,4-Trimethylpentane, or Carbon tetrachloride) at T = 293.15 K. *J. Chem. Thermodyn.* **1997**, *29*, 853−863.

(10) Marsh, K. N. *TRC Data Bases for Chemistry and Engineering-TRC Thermodynamic Tables*; Texas A&M University: College Station, TX, 1995.

(11) Vargaftik, N. B. *Handbook of the Thermophysical Properties of Liquids and Gases*; FM: Moscow, 1963.

(12) Postigo, M.; Mariano, A.; Mussari, L.; Canzonieri, S. Viscosities for Binary Mixtures of 1-Decanol, Hexane, and Diethylamine at 10, 25, and 40 °C. *J. Solution Chem.* **2001**, *30*, 1081−1090.

(13) Heintz, A.; Schmittecker, B.; Wagner, D.; Lichtenthaler, N. Excess Volumes of Binary 1-Alkanol/Hexane Mixtures at Temperatures between 283.15 and 323.15 K. *J. Chem. Eng. Data* **1986**, *31*, 487−492.

(14) Krestov, G. A.; Afanasiev, W. N.; Jefriemova, L. S. *Physicochemical Properties of Binary Solvents*; Khimia: Leningrad, 1988.

(15) *TRC Thermodynamic Tables. Hydrocarbons*; Thermodynamics Research Center: College Station, TX, 1996.

(16) Daridon, J. L.; Lagourette, B.; Grolier J.-P. E. Experimental Measurements of the Speed of Sound in *n*-Hexane from 293 to 373 K and up to 150 MPA. *Int. J. Thermophys.* **1998**, *19*, 145−160.

(17) Khasanshin, T.; Shchemelev, A. Speed of Sound in Liquid *n*-Alkanes. *High Temp.* **2001**, *39*, 60−68.

(18) Ye, S.; Lagourette, B.; Alliez, J.; Saint-Guirons, H.; Xans, P.; Montel, F. Speed of Sound in Binary Mixtures as a Function of Temperature and Pressure. *Fluid Phase Equilib.* **1992**, *74*, 177−202.

(19) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

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