SOME THERMODYNAMIC PROPERTIES OF n-HEPTANE ON THE SATURATION LINE

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The results of measurements of the speed of sound in n-heptane on the saturation line are presented. The values obtained are used to calculate a series of thermodynamic quantities.

The study of the thermodynamic properties of liquids over a broad interval of temperatures and pressures is of undoubted theoretical and applied interest. However, because of the experimental difficulties, the thermodynamic properties of only a few liquids have been thoroughly studied.

As a means of investigation, acoustic methods are notable for their relative simplicity and reasonable accuracy. A knowledge of the speed of sound makes it possible to calculate such important thermodynamic quantities as the adiabatic β_s and isothermal β_t compressibilities, the specific heats at constant pressure c_p and constant volume c_v, and their ratio $\gamma = c_p/c_v$.

We have measured the speed of ultrasound in the liquid phase of n-heptane on the saturation line in the temperature interval 20-266°C. The measurements were made on a pulsed ultrasonic apparatus at a frequency of 1 MHz using the method of a single fixed distance. An autoclave with the test liquid was placed in an air heater with an electronic thermoregulator and kept at a given temperature for the time needed to establish the equilibrium state (6-8 h near the critical point). The temperature was measured with a platinum resistance thermometer introduced into the autoclave near the acoustic path. The accuracy of the temperature measurements was 0.1°C. The error in determining the speed of sound was ±2 m/sec.

For investigation purposes we took a sample of n-heptane with the following characteristics: $\rho_4^{20} = 0.6837$; $n_D^{20} = 1.3878$; $t_{bp} = 98.4$°C (760 mm Hg).

TABLE 1. Speed of Sound in n-Heptane along the Saturation Line

t, °C	c, m/sec: authors' measurements	c, m/sec: published data	t, °C	c, m/sec
20	1155	1154 [1]	150	620
		1148 [2]	160	580
30	1112	1112 [1]	170	540
		1107,5 [2]	180	500
40	1069	1070 [1]	190	459
		1062,2 [2]	200	417
50	1027	1028 [1]	210	374
		1022 [2]	220	330
60	985	981 [2]	230	285
70	943	940 [2]	240	236
80	903		250	184
90	862		260	122
100	821		265	85
110	782		266	77
120	741			
130	701			
140	660			

TABLE 2. Thermodynamic Properties of n-Heptane on the Saturation Line

t, °C	$\beta_s \cdot 10^{11}$, m^2/N	$\beta_t \cdot 10^{11}$, m^2/N	$c_p \cdot 10^{-3}$ J/kg·deg	$c_v \cdot 10^{-3}$, J/kg·deg	γ
20	109,7	138,8	2,227	1,759	1,266
30	119,8	151,4	2,265	1,792	1,264
40	131,3	165,7	2,303	1,825	1,262
50	144,1	181,4	2,345	1,863	1,259
60	158,8	199,6	2,386	1,898	1,257
70	175,7	220,3	2,428	1,936	1,254
80	194,3	243,3	2,474	1,976	1,252
90	216	270	2,520	2,019	1,248
100	242	302	2,571	2,062	1,247
110	271	339	2,621	2,097	1,250
120	307	384	2,671	2,130	1,254
130	350	438	2,721	2,172	1,253
140	402	504	2,776	2,214	1,254
150	465	585	2,830	2,250	1,258
160	542	681	2,880	2,299	1,256
170	640	807	2,947	2,337	1,261
180	764	972	3,006	2,365	1,271
190	937	1201	3,068	2,393	1,282
200	1164	1502	3,135	2,423	1,294
210	1492	1966	3,206	2,432	1,318
220	1989	2703	3,294	2,424	1,359

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The results of the measurements are presented in Table 1 and compared with the most accurate published values [1, 2].

The results obtained for the speed of sound and the known values of the density ρ [3], the saturated vapor pressure P [3, 4] and the specific heat at constant pressure [3, 5] enabled us to calculate the adiabatic and isothermal compressibilities, the specific heat at constant volume, and the ratio of specific heats.

The adiabatic compressibility was calculated from the known equation

$$\beta_s = \frac{1}{\rho c^2}\,.$$

The joint solution of the equations

$$\gamma = 1 + \frac{c^2 \alpha_p^2 T}{c_p}$$

and

$$\alpha_p = \alpha_s + \gamma\beta_s \frac{dP}{dT}\,,$$

where α_p and α_s are the coefficients of thermal expansion at constant pressure and on the saturation line, respectively, enabled us to determine the quantity γ. The values of γ thus calculated were used to compute the isothermal compressibility $\beta_t = \gamma\beta_s$ and the specific heat at constant volume $c_v = c_p/\gamma$. The results are presented in Table 2.

Analysis of the results reveals certain features of the temperature variation of the thermodynamic properties of n-heptane along the saturation line. In particular, γ has a weakly expressed minimum at the boiling point. It should be noted that during the interval 20-80°C the variation of γ with temperature is so small (1-2%) that for approximate calculations this quantity may be assumed to be independent of the temperature. At higher temperatures γ increases appreciably. The specific heat c_v increases with temperature.

It may be assumed that these features of the temperature behavior of γ and c_v will also be observed in connection with other liquids having similar chemical structure and physical properties, in particular, other members of the n-paraffin homologous series.

NOTATION

- c is the speed of sound;
- β_s is the adiabatic compressibility;
- β_t is the isothermal compressibility;
- c_p is the specific heat at constant pressure;
- c_v is the specific heat at constant volume;
- γ is the ratio of specific heats;
- ρ is the density;
- n_D is the index of refraction;
- P is the vapor pressure;
- T is the absolute temperature;
- α is the coefficient of volume expansion.

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