STUDY OF THE EQUILIBRIUM PROPERTIES OF HYDROCARBONS ON THE SATURATION LINE BY AN ACOUSTIC METHOD

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The ultraacoustic method is now being widely employed for studying the physicochemical properties of materials. By using experimental data relating to the velocity of sound C, the density ρ, and the specific heat at constant pressure C_p, many important thermodynamic parameters (β_S, β_T, γ, C_V etc.) may be calculated. In this paper we shall present the results of measurements made on the velocity of sound in five liquid-phase hydrocarbons (pentene-1, hexene-1, n-hexane, n-heptane, and toluene) on the saturation line between −120 and +310°C. Altogether we have studied 22 hydrocarbons belonging to various homologous series: n-alkanes, 1-alkenes, and aromatic hydrocarbons. The parameters of the liquids considered in this paper are presented in Table 1.

The measurements were carried out in the pulse-type ultrasonic installation described in [1]. The temperature was measured with a platinum resistance thermometer placed directly in the test liquid (accuracy 0.1°C). In the low-temperature range a cryostat based on liquid nitrogen was employed. The error in determining the velocity of sound (allowing for scaling inaccuracies) was no greater than 1-3 m/sec.

The resultant velocity-of-sound data were used, together with the experimental values of the density ρ [2-7], saturated vapor pressure P [1, 8-9], and specific heat at constant pressure C_p [2, 3, 10-16], to calculate the adiabatic and isothermal compressibilities β_S and β_T and the ratio of the specific heats γ. The error in determining β_S, β_T, and γ was, respectively, 0.5-1.5, 1-3, and 1.5-5%. The results of the calculations, and also the experimental data relating to the velocity of sound, are presented in Table 2.

Analysis of the results showed that the isothermal compressibility β_T of the n-alkanes and 1-alkenes closely obeyed the equation

$$\beta_T C^n = a + bt,$$

where C is the velocity of sound in m/sec, t is the temperature in °C, n=2.5, and a and b are constants. For hydrocarbons of the same series the quantity a falls regularly with increasing number of the homolog, while b is approximately the same for all terms of the series. The values of the coefficients a and b obtained by the method of least squares are given in Table 1. The mean error in the calculation of β_T by means of the foregoing equation is no greater than 1-2%.

On passing from one homolog to another in the n-alkanes, 1-alkenes, and alkyl benzenes, the velocity of sound increases and the adiabatic and isothermal compressibilities diminish. This is evidently because of the increasing intensity of the intermolecular forces which occurr with increasing number of the homolog.

TABLE 1

Hydrocarbon	ρ_4^{20}, g/cm³	n_D^{20}	t_b, °C (760 mm Hg)	a, $m/sec^{2.5}$/bar	b, $(m/sec)^{2.5}$/bar·deg
Pentene 1	0,6410	1,3716	30,2	6977	−6,2
Hexene 1	0,6733	1,3880	63,6	6583	−6,4
m-Hexane	0,6591	1,3751	68,7	6573	−4,4
m-Heptane	0,6837	1,3878	98,4	6396	−4.9
Toluene	0,8666	1,4966	110,6	—	—

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TABLE 2

T, °C	c, m/sec	$\beta_S\cdot10^6$, bar^{-1}	$\beta_T\cdot10^6$, bar^{-1}	γ	c, m/sec	$\beta_S\cdot10^6$, bar^{-1}	$\beta_T\cdot10^6$, bar^{-1}	γ
	Pentene 1				Hexene 1			
—100	1664	47,8	66	1,38	1687	45,2	60	1,34
—80	1549	56,5	79	1,38	1582	52,4	70	1,34
—40	1331	80,7	112	1,38	1379	72,3	96	1,33
0	1125	120	165	1,38	1187	103	136	1,32
40	927	188	258	1,37	1005	151	198	1,31
80	735	324	447	1,38	829	237	308	1,30
100	639	448	620	1.38	742	307	400	1,30
140	447				569	570	740	1,30
180	217				391	1360	1820	1,34
200					293	2660	3700	1,39
	n-Hexane				n-Heptane			
—80	1585	53,5	69,6	1,30	1622	49,7	63,6	1,28
—40	1382	73,6	95,7	1,30	1425	67,1	85,9	1,28
0	1189	105	135	1,29	1241	92,7	118	1,27
40	1010	153	198	1,29	1067	131	166	1,26
80	834	239	309	1,29	901	194	243	1,25
100	747	308	397	1,29	820	242	302	1,25
140	573	570	747	1,31	660	402	504	1,25
180	393	1360	1860	1,37	499	765	972	1,27
200	296	2620	3760	1,44	416	1160	1500	1,29
240					236	4300	6500	1,51
	Toluene							
—80	1818	31,5	45,2	1,44				
—40	1613	41,7	58,4	1,40				
0	1417	56,2	76,8	1.37				
40	1240	76,7	103	1,34				
80	1074	107	142	1,33				
100	995	128	169	1,31				
140	842	189	250	1,30				
180	691	300	393	1,31				
200	615	393	519	1,32				
240	462	763	1050	1,37				
280	296	2140	3190	1,49				
300	200	—	—	—				

The ratio of the specific heats γ or the n-alkanes and 1-alkenes varies very little between the melting point t_m and 0.85 of the critical temperature.

It was shown earlier [17] that for many physical properties of the n-alkanes and alkylbenzenes a relation of the following kind was closely satisfied:

$$\frac{y_1}{y_2} = \text{const} \text{ for } T'_* - T_1 = T''_* - T_2,$$

where y_1 and y_2 are the properties of homologs 1 and 2 under consideration at certain temperatures T_1 and T_2, respectively, while T'_* and T''_* are the critical temperatures. This relationship holds for the substances considered in the present investigation.

LITERATURE CITED

1. Yu. A. Neruchev, V. V. Zotov, and N. F. Otpushchennikov, "Velocity of sound in n-nonane," Ukr. Fiz. Zh., 13, 692-693 (1968).
2. N. B. Vargaftik, Handbook on the Thermophysical Properties of Gases and Liquids [in Russian], GIFML, Moscow (1972).
3. J. Timmermans, Physicochemical Constants of Pure Organic Compounds, Vol. 2, American Elsevier (1965).
4. R. A. Orwol and P. J. Flory, "Equation-of-state parameters for normal alkanes. Correlation with chain length," J. Amer. Chem. Soc., 89, No. 26, 6814-6822 (1967).
5. H. O. Day and W. A. Felsing, "The compressibility of pentene-1," J. Amer. Chem. Soc., 73, No. 10, 4839-4840 (1951).
6. "Selected values of physical and thermodynamic properties of hydrocarbons and related compounds," APJ Research Project 44, Pittsburgh, Pennsylvania (1953).

7. B. N. Kireev, "Determination of the density of olefins on the saturation line," in: Ultrasound and the Physicochemical Properties of Materials [in Russian], No. 7, Izd. Kursk. Ped. Inst., Kursk (1973), pp. 40–45.
8. Handbook of Chemistry [in Russian], Vol. 1, Goskhimizdat, Moscow–Leningrad (1962).
9. T. R. Das and N. R. Kuloor, "Thermodynamic properties of hydrocarbons: Part XI – 1-pentene," Indian J. Technol., 5, No. 4, 113–118 (1967).
10. Y. S. Touloukian, Thermophysical Properties of Matter. Specific Heat of Nonmetallic Liquids and Gases, Vol. 6, Washington (1970).
11. W. S. Tamplin and D. A. Zuzic, "Specific heat of organic hydrocarbons," Hydrocarb. Proc., 46, No. 8, 145–146 (1967).
12. J. E. Messerly, G. B. Guthrie, S. S. Todd, and H. L. Finke, J. Chem. Engng. Data, 12, No. 3, 338 (1968).
13. W. G. Schlinger and B. H. Sage, "Isobaric heat capacity of 1-butene and 1-pentene," Ind. Eng. Chem., 41, 1779–1782 (1949).
14. S. S. Todd, G. D. Oliver, and H. M. Huffman, J. Amer. Chem. Soc., 69, No. 6, 1519–1525 (1947).
15. Kh. I. Amirkhanov, B. G. Alibekov, D. I. Vikhrov, V. A. Mirskaya, and L. N. Levina, "Isobaric specific heat of n-pentane, n-hexane, n-heptane, and n-octane along the liquid boundary curve," Teplofiz Vys. Temp., No. 6, 1310–1313 (1971).
16. T. S. Akhundov and R. A. Eksaev, "Experimental determination of the isobaric specific heat of liquid toluene at 30–300°C for pressures up to 260 bars," Izv. Vyssh. Uchebn. Zaved., Neft' i Gaz, No. 2, 68–72 (1973).
17. Yu. A. Neruchev, V. V. Zotov, and N. F. Otpushchennikov, "Velocity of sound in the homologous series of n-paraffins," Zh. Fiz. Khim., 43, No. 11 2843–2845 (1969).