The speed of sound and thermophysical properties of isomers of hexane

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Abstract. The results of measurements of sound velocity and density in the liquid phase isomers of hexane. The influence of molecular structure on the energy of intermolecular forces.

1. Introduction

The problems of the liquid state of substance as before attract the attention of researchers. The absence of universal equations of the liquid state matter, the nature of intermolecular forces and features of liquid structure, physical nature of the critical state of matter represent targets theoretical and experimental research.

The particular interest represents experimental and theoretical studies of the simplest systems, which include the isomers of hexane [1]. Accepting the identity nature of intermolecular forces in hydrocarbons and the atom-atom interaction mechanism can consider issue of the influence geometrical forms molecules isomers on their thermal properties.

The geometrical features structure of molecules isomers can be seen in Fig. 1. As follows from Fig. 1 in comparison with the molecule of n-hexane, the molecules are isomers the more “compact” and less symmetrical. “Compactness” increases towards n-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane.

![Figure 1. The structure of the molecules of the isomers of hexane](image)

The hexane isomers have almost similar boiling temperatures, critical temperatures and critical densities. However, their crystallization temperatures differ markedly each other. They are significantly lower in isomers with more non-symmetrical molecules. The difference of the crystallization temperatures of isomers reaches 60° or more. [2]. Researches indicate carried out that this effect may indicate the existence specific type of hydrogen bonds between C−H⋯H−C groups of the neighboring molecules. The existence of such hydrogen bonds is discussed for example, in [2, 3, 4]. Their existence is explained by presence “charge transfer”[2].
2. Experimental section

For the study we use samples 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane and n-hexane that given by the company “Merck Schuchardt”. Their purity was above 99.5%. It was controlled by measuring density and refractive index before and after measurements. We measured the speed of sound and density.

The speed of sound in the liquid phase of isomers hexane was measured by pulse-phase method in without dispersive region on a frequency of 1 MHz on the apparatus developed in the laboratory of molecular acoustics scientific research center the physics of condensed matter, Kursk state University [5, 6, 7] certified by the Russian service of standard reference data “Standartinform” [8]. Autoclave high pressure with the tested liquid, was constructed by the authors, that placed in a thermostat “Thermeks” Russia, which maintained the set temperature within 0.01°C. The temperature of the liquid was measured by 100-Ohm platinum resistance thermometer placed into the test liquid, the converter signals “Terkon” company “Thermeks” Russia with accuracy of 0.05°C and additionally was controlled by the model platinum resistance thermometer immersed into the body autoclave.

The speed of sound on saturation line in the investigated liquids was measured in the region from -30°C to critical points. Due to abnormally high absorption of the ultrasound signal the value of the speed of sound near critical point measure failed.

Analysis of factors are affecting the of the measurements lead to the conclusion that the uncertainty of the obtained values of the sound speed in the studied temperature interval don’t exceed $\pm \frac{1m}{s}$.

At the same time, in the investigated substances in the range of -30°C to +60°C at atmospheric pressure was measured density. The uncertainty of the obtained density values is not greater than 0.05%.

3. Results and Discussion

The obtained data on the speed of sound and density together with literature data [2] on the heat capacity and vapor pressure on saturation line were used to calculate the thermophysical properties and the energy of intermolecular forces $|E_p|$ studied substances (tables 1-3). For that were used well known relations of thermodynamics and the equation of state [1, 9], which presented below

$$ T \left( \frac{\partial p}{\partial T} \right)_V = \frac{|E_p|}{V} + \frac{NkT}{V}. $$

Equation (1) follows that the full pressure in the condensed system is determined by the sum of two terms, one of which represents the density energy of intermolecular forces and the other is the density flux pulses of particles. It does not contain empirical parameters and allows studying the structure liquids and the nature intermolecular forces.

As shown our investigations [4, 5, 6, 7, 10], in the liquid phase of hydrocarbons is dominated the dispersion attraction forces $(m = 6)$, the energy of which is proportional to the square density. The contribution to the total interaction energy of repulsive forces $(n = 12)$ is noticeable only in the low temperature region where very large liquid density. However, a comprehensive description of the thermophysical properties are of liquids is possible only when take into account the energy of long-range “hydrogen” bonds whose energy is proportional to $\rho^{1/3}$.

Confirmation of this can serve the next formula

$$ |E_p| = B\rho^2 + b\rho^{1/3}(1 - (\rho/\rho_b)^{1/3}). $$

This formula is well executed in a wide temperature range from boiling points to the points of crystallization hydrocarbons. Equation (2) indicates that the interaction energy of the molecules on
saturation line is determined by three types of forces. However, at the temperature region above the normal boiling temperature the energy of hydrocarbons on saturation line is determined by one term, representing the energy of the dispersion forces. At approaching the critical point because of the intensive decay of dimeric structures hydrocarbons “visualized” “hydrogen” bonds, the energy of which is determined by the same ratio

\[ E_{\text{bond}} \approx b \rho^{3/3}. \]

The constants of dispersion forces \( B \) and bonding forces \( b \) are determined by the critical parameters substance with the help relations

\[ B = \frac{T_k \left( \frac{\partial \rho}{\partial T} \right)_p}{\rho_k^{3/3}} \]

\[ b = \frac{RT_k}{2M \rho_k^{3/3}} \]

These formulas are deduced directly from equations (1) and the decay condition of dimers \( e_b = kT_1 \).

This, as we believe, represents a critical transition liquid-vapor.

Considering that in addition to traditional intermolecular forces (dispersion forces of attraction \((m = 6)\) and short-range repulsive forces \((n = 12)\) ) in the organic media, there are the long-range “weak” chemical bonds of donor-accepted type, representing the “hydrogen” bonds [11] between neighboring \( C - H \ldots H - C \) groups, for estimating the energy of intermolecular forces \( |E_p| \) we were used the ratio (2) and data [2, 12]. The all results are presented in tables 1-3.

| \( T, °K \) | \(|E_p|, (2) \text{kJ/kg} \) | \( \Delta E \) [2] | \( T, °K \) | \(|E_p|, (2) \text{kJ/kg} \) | \( \Delta E \) [2] |
|---|---|---|---|---|---|
| 183,15 | 402,0 | 420,9 | 273,15 | 367,8 | 355,3 |
| 193,15 | 410,8 | 413,4 | 283,15 | 359,8 | 348,1 |
| 203,15 | 408,0 | 405,9 | 293,15 | 351,4 | 340,9 |
| 213,15 | 404,3 | 398,6 | 303,15 | 342,5 | 333,5 |
| 223,15 | 399,8 | 391,3 | 313,15 | 333,3 | 326,0 |
| 233,15 | 394,6 | 384,0 | 323,15 | 323,7 | 318,4 |
| 243,15 | 388,8 | 376,8 | 333,15 | 313,9 | 310,7 |
| 253,15 | 382,3 | 369,7 | 343,15 | 304,0 | 303,0 |
| 263,15 | 375,3 | 362,5 | | | |

**Table 1.** The energy of intermolecular forces calculated for n-hexane

| \( T, °K \) | \(|E_p|, (2) \text{kJ/kg} \) | \( \Delta E \) [2] | \( T, °K \) | \(|E_p|, (2) \text{kJ/kg} \) | \( \Delta E \) [2] |
|---|---|---|---|---|---|
| 120 | 451,7 | 460,1 | 230 | 372,5 | 367,9 |
| 130 | 444,0 | 449,9 | 240 | 365,6 | 360,7 |
| 140 | 436,4 | 440,3 | 250 | 358,7 | 353,6 |
The joint effect of these forces leads to association

From obtained results follows that the increase “compactness” molecules of isomers leads an

| T, °C | ρ, kg/m³ | u, m/c | |Ep| (1), kJ/kg | |Ep| (2), kJ/kg | ρ, kg/m³ | u, m/c | |Ep| (1), kJ/kg | |Ep| (2), kJ/kg |
|------|----------|--------|----------------|----------------|----------|--------|----------------|----------------|
| -30  | 697,3    | 1299,8 | 364            | 364            | 705,5    | 1317,9 | 361            | 363            |
| -25  | 693,0    | 1276,0 | 361            | 361            | 701,6    | 1294,7 | 359            | 360            |
| -20  | 688,6    | 1252,3 | 359            | 357            | 697,7    | 1271,6 | 357            | 357            |
| -15  | 684,3    | 1228,6 | 356            | 354            | 693,7    | 1248,5 | 354            | 354            |
| -10  | 679,9    | 1205,1 | 353            | 350            | 689,6    | 1224,5 | 352            | 350            |
| -5   | 675,5    | 1181,6 | 349            | 347            | 685,5    | 1202,4 | 349            | 347            |
| 0    | 671,1    | 1158,2 | 346            | 343            | 681,3    | 1179,4 | 346            | 344            |
| 5    | 666,6    | 1134,9 | 342            | 339            | 677,0    | 1156,5 | 343            | 340            |
| 10   | 662,1    | 1111,7 | 339            | 336            | 672,7    | 1133,6 | 340            | 337            |
| 15   | 657,6    | 1088,5 | 335            | 332            | 668,3    | 1110,7 | 337            | 334            |
| 20   | 653,1    | 1065,5 | 331            | 329            | 663,9    | 1087,9 | 333            | 330            |
| 25   | 648,5    | 1042,5 | 327            | 325            | 659,4    | 1065,2 | 330            | 327            |
| 30   | 643,9    | 1019,5 | 322            | 321            | 654,8    | 1042,5 | 326            | 323            |
| 35   | 639,3    | 996,7  | 318            | 318            | 650,2    | 1019,9 | 322            | 319            |
| 40   | 634,6    | 973,9  | 313            | 314            | 645,6    | 997,3  | 319            | 316            |
| 45   | 629,8    | 951,2  | 309            | 310            | 641,0    | 974,8  | 314            | 312            |
| 50   | 625,0    | 928,6  | 304            | 307            | 636,4    | 952,3  | 310            | 309            |
| 55   | 620,2    | 906,0  | 299            | 303            | 631,8    | 929,9  | 306            | 305            |
| 60   | 615,3    | 883,5  | 294            | 299            | 627,3    | 907,4  | 301            | 302            |

Table 2. The energy of intermolecular forces calculated for 2-methylpentan

| T, °C | ρ, kg/m³ | u, m/c | |Ep| (1), kJ/kg | |Ep| (2), kJ/kg |
|------|----------|--------|----------------|----------------|
| -30  | 697,3    | 1299,8 | 364            | 364            |
| -25  | 693,0    | 1276,0 | 361            | 361            |
| -20  | 688,6    | 1252,3 | 359            | 357            |
| -15  | 684,3    | 1228,6 | 356            | 354            |
| -10  | 679,9    | 1205,1 | 353            | 350            |
| -5   | 675,5    | 1181,6 | 349            | 347            |
| 0    | 671,1    | 1158,2 | 346            | 343            |
| 5    | 666,6    | 1134,9 | 342            | 339            |
| 10   | 662,1    | 1111,7 | 339            | 336            |
| 15   | 657,6    | 1088,5 | 335            | 332            |
| 20   | 653,1    | 1065,5 | 331            | 329            |
| 25   | 648,5    | 1042,5 | 327            | 325            |
| 30   | 643,9    | 1019,5 | 322            | 321            |
| 35   | 639,3    | 996,7  | 318            | 318            |
| 40   | 634,6    | 973,9  | 313            | 314            |
| 45   | 629,8    | 951,2  | 309            | 310            |
| 50   | 625,0    | 928,6  | 304            | 307            |
| 55   | 620,2    | 906,0  | 299            | 303            |
| 60   | 615,3    | 883,5  | 294            | 299            |

Table 3. The energy of intermolecular forces of isomers n-hexane

$\Delta \varepsilon$ – the differences intrinsic energies of liquid and vapor phases according [2].

From obtained results follows that the increase “compactness” molecules of isomers leads an increase the distances between the interacting centers. As a result, the dispersion constants are decreasing from 0.81 – n-hexane; 0.79 – 2-methylpentan; 0.77 – 3-methylpentan to 0.74 – 2,2-dimethylbutane. Naturally, this effect also contributes to lowering the crystallization temperatures of homologues. However, the process of crystallization, as we believe, is caused other forces – with the forces of bond between the $C-H...H-C$ groups. The joint effect of these forces leads to association of molecules which is more efficient in case of symmetric molecules. This may explain the extremely
low temperature crystallization of squalane [13] molecules of which, in fact, represent a hydrocarbon “tangles”.

4. Conclusion
1. The intermolecular interactions in hydrocarbon media are characterized by three types of forces: 1) dispersion forces attraction \((m = 6)\); 2) short-range repulsive forces \((n = 12)\); 3) the “weak” long-range “hydrogen” bonds of donor-acceptor type.
2. The main contribution to the energy intermolecular of the isomers hexane as of the other hydrocarbons belong the dispersion forces of attraction, the energy of which is proportional to the square of density. Their values \(B\) decrease with increasing “compactness” of molecules.
3. The “hydrogen” bonds \(C−H...H−C\) groups cause association of hydrocarbon molecules. These “long-range” bonds and space molecular structure determine the magnitude temperature crystallization of homologs.

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