

THE MOLECULAR CHARACTERISTICS OF OIL FRACTIONS DETERMINED FROM ULTRASONIC VELOCITY MEASUREMENTS

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This paper presents the results of measurements of ultrasonic velocity in liquid hydrocarbon multi-fraction fuels and individual hydrocarbons, on the basis of which the Rao constants, the mean distances between the surfaces of the free molecules, the Langemann constants, and the acoustic diameters of the molecules were determined. The dependencies of the acoustic constants, the distances between the molecules and the acoustic diameters of the molecules on the density and on the molecular mass for different fractions of fuels and different individual hydrocarbons are presented. It was found that the quantities used in molecular acoustics can be used to characterize the properties of multi-component hydrocarbon mixtures and to identify their structure. The results of the investigations confirmed the usefulness of the concept presented in this paper — the concept of the inclusion of the intermolecular interaction forces by a change in the acoustically determined intermolecular distances in a hypothetical equivalent single — component liquid.

Notation

- A, a, B, b — characteristic constants of a homologous series of hydrocarbons
- C_A — content of aromatic carbon (in %)
- C_N — content of naphthene carbon (in %)
- C_P — content of paraffin carbon (in %)
- c — ultrasonic propagation velocity
- d_a — acoustic molecule diameter
- d_{ref} — molecule diameter determined from refraction
- J — mean distance between surfaces of free molecules
- K — constant
- K_A — number of aromatic rings
- K_N — number of naphthene rings
- K_o — total number of rings
- K_s — modulus of isentropic compressibility
- L — Lagemann's constant

M	— molecular weight
N	— Avogadro's number
n	— optical refractive index at the D line
R	— Rao's constant
S	— sulphur content
T	— temperature
T_k	— solidification temperature
T_z	— ignition temperature
V	— volume
V_M	— molar volume
W	— Rao's constant
β_s	— coefficient of isentropic compressibility
ρ	— density
ρ_0	— reference density
T	— density at the temperature of the investigation
ν	— kinematic viscosity

1. Introduction

The ultrasonic velocity and its relation to the density of a liquid permits information to be obtained on the chemical and physical structure of the liquid. The relation of these quantities to the molecular weight and the specific heat make it possible to determine the interaction forces, and the volumes and diameters of relevantly defined molecules, etc. The additivity of ultrasonic velocities in the case of liquid mixtures, which has been investigated by different workers [1, 8, 15], permits knowledge obtained about the physical structure, the solubility, and the accompanying dilatation effects to be evaluated. The use of the ultrasonic velocity for structural analysis and the determination of the physical and chemical properties of simple hydrocarbon mixtures, fractions, and products from crude oil has been limited to date. The investigations of CORNELISSON, WATERMAN, HARVE [2], for example, dealt with the relations between the viscosity, the optical refractive index, the surface tension, and the ultrasonic velocity (ν - n - c and ν - c - b), and the dependence of ultrasonic velocity on density for fractions of mineral oils. These papers had a fundamental character and were limited to saturated oil fractions. There is a lack, however, of detailed information on the relation of the ultrasonic velocity to the constitutional properties of fractions of crude oil: fuels, oils, etc. The investigations of the utilitarian properties of the products have been limited to the determination of the elastic constants — moduli and coefficients of adiabatic compressibility — and, more recently, of the density.

The present paper presents the results of measurements of the ultrasonic velocity and its relation to the molecular weight and density of multi-component hydrocarbon mixtures and fractions which are components of oil fuels.

The essential difficulty in the investigation of mixtures of this type, and in particular, the hydrocarbon fractions, is not only a lack of an equation of

state for the real liquid, but also of mixing principles. In the case of real liquids these principles exist only for two-component and sometimes three-component systems. Thus all the quantities, which are measured relatively, are determined by mean values. Of necessity the problem of mixtures is reduced to a hypothetical one-component liquid. Each molecular interpretation, both of the measurement data and of the material constants, including rheological models, also applies to this kind of liquid. How, therefore, should such quantities as the optical refractive index, the molecular weight, and particularly the molecular diameter, the intermolecular distance or the coefficient of compressibility be interpreted? Of necessity the only possibility is the use of the model of the mean liquid mentioned above. This involves, according to the present authors, the assumption of the unambiguous definition of a molecule of such a one-component mean liquid. From the point of view of molecular physical chemistry and mathematic correctness, the closest solution is the assumption of a molecule diameter which is defined on the basis of the statistical theory of liquids. This will be a space in which the probability of the existence of a molecule with a complex of interactions is equal to unity. Certainly for such a simple model, for the interpretation of phenomena related to wave propagation, it can be assumed that long-range interactions are represented by changes in the molecule diameter and the intermolecular distance. Accordingly a lack of intermolecular interaction can be assumed in a model of such a liquid. The model of ultrasonic wave propagation becomes simplified, and the velocity can be regarded as the sum of the wave propagation velocities in the intermolecular space, and inside the molecule.

The above gross approximations can, for the purposes of the understanding and description of multi-component mixtures, use the characteristic quantities defined by optical and dilatometric methods, and by the methods of molecular acoustics.

2. Relations and characteristic constants

The basic constitutional quantity of liquid organic compounds, which links the ultrasonic velocity and the density, is the coefficient or modulus of isentropic compressibility

$$\beta_s = \frac{1}{K_s} = \frac{1}{\rho c^2}. \quad (1)$$

In liquids the quantities c and ρ decrease as the temperature decreases, with the exception of water and some mixtures of strongly polarized compounds. This is described, for example, by the known Rao relation [11, 12]

$$R = \sqrt[3]{\frac{M}{\rho c}} = \text{const.} \quad (2)$$

The significance of the quantity R , the so called molar sound velocity, results from its additive and constitutional properties. For most organic solutions, liquid chemical elements, and some mixtures, the constant R is usually independent of temperature. Over a moderate temperature range relation (2) is satisfied for some nonassociated liquids. There is, however, a group of organic compounds, e.g. paraffin or the aromatic hydrocarbons in crude oil, for which $R \neq \text{const.}$

In the case of oil hydrocarbons it is interesting to note the change of the quantity R in a homologous series and in mixtures of their components, and the dependence on P and T . The investigation of relation (2) as a function of molar mass has shown in many cases a linear character [12]:

$$R = aM + b. \quad (3)$$

For aliphatic hydrocarbons the values of a and b in equation (3) are respectively 13.97 and 155, while for aromatic hydrocarbons they are 14.02 and 120 [1]. The opinion has been voiced in the literature that the constant a is practically the same for different homologous series [11, 12].

For a number of liquids the expression $e\sqrt[7]{\beta_s}$ takes constant values over a wide range of pressure and temperature [12]. This expression in the form of the relation

$$W = \frac{M}{e\sqrt[7]{\beta_s}} \quad (4)$$

is known as the molar compressibility. From relations (1), (2) and (4) the following relation can be obtained

$$W = M^{1/7} R^{6/7}. \quad (5)$$

For nonassociated liquids the quantity W is also constant and should satisfy the condition of invariability better than does the constant R . This was confirmed in paper [10] for binary hydrocarbon mixtures of different concentrations. For most mixtures the following linear relation exists

$$W = AM + B. \quad (6)$$

For mixtures containing both "lighter" and "heavier" components, relation (6) is rectilinear, while relation (3) is not. The rectilinearity of relation (3) occurs with the introduction of equimolar volumes, while relation (6) is rectilinear in practically all cases.

In addition to the constants mentioned above another equation, proposed by Lagemann, may be used [1, 12]

$$L = \frac{\Delta c}{\Delta T} \sqrt{M} = \text{const.} \quad (7)$$

This is satisfied by many organic liquids and their mixtures. In the region of considerable change in the temperature coefficient of sound velocity, i.e.

near the critical and solidification temperatures, this relation is not satisfied [1, 12].

Knowing the temperature coefficient of the sound velocity and the coefficient of expansion, the density and the molecular weight, it is possible to define the acoustic diameter of the molecule [7]. This diameter may be interpreted as being close to the statistical molecular diameter. The acoustic molecular diameter can be defined, for example, using the following relation [7]

$$d_a = \frac{\frac{1}{c} \left(\frac{dc}{dT} \right)_P}{\frac{1}{c} \left(\frac{dc}{dT} \right)_P - \frac{1}{3} \frac{1}{V} \left(\frac{dV}{dT} \right)_P} \left(\frac{M}{\rho N} \right)^{1/3} \quad (8)$$

Assuming a spherical shape for the molecule JACOBSON gave a relation permitting the determination of the distance between the surfaces of the free molecules [5, 6]

$$J = \frac{K}{\rho^{1/2} c}, \quad (9)$$

where $K = \text{const}$ for $T = \text{const}$.

By analogy with an ideal gas, the quantity J can thus be regarded as the free path. As for the molar sound velocity, this quantity, in view of its dimension, is interesting for interpretation only. The values of K for different temperatures are the following: 0 °C — 588; 10 °C — 604; 20 °C — 618; 30 °C — 631; 40 °C — 624; 50 °C — 652 [10].

3. Procedure

The hydrocarbon mixtures analyzed were separated in the form of fractions of the oil fuels: jet fuel (1) and Diesel fuel (2, 3, 4, Tables 1 and 2) [9].

Some of these fractions were represented by only one kind of structure, in other a specific kind of structure dominated [9]

- I — n -isoparaffin and naphthene fractions,
- II — n -paraffin fractions,
- III — isoparaffin and naphthene fractions,
- IV — isoparaffin and naphthene fractions with a majority of naphthene fractions,
- V — isoparaffin and naphthene fraction with a majority of isoparaffin fractions,
- VI — aromatic unicyclic fractions, $n^{20} = 1.48 + 1.53$,
- VII — aromatic polycyclic fractions, $n^{20} > 1.53$.

The method of separating the fractions is described in reference [19]. Using the methods of liquid and column chromatography, fractions I, VI and

Table 1. The standard properties of fuels

Properties	Sample			
	1	2	3	4
ρ_{4}^{20}	0.8150	0.8371	0.8412	0.8484
distillation [°C]				
beginning	148	—	—	—
10%	158	—	—	250
50%	193	—	—	—
90%	242	—	—	—
98%	270	—	—	—
up to 300 °C	—	74%	50%	68%
up to 350 °C	—	95%	85%	92%
ν^{20} [cSt]	1.63	4.84	5.51	7.23
T_k^* [°C]	-60	-14.5	-13.0	-6.0
T_z^* [°C]	36 M.P.	80 M.C.	60 M.C.	36 M.P.
S [%]	0.029	0.271	0.650	0.372

Table 2. The physical and chemical properties and the structural composition of the fractions separated from the fuels

Fraction	T_k	ρ_4^{20}	M	n^{20}	C_P	C_A	C_N	K_0	K_A	K_N
I -1	-60	0.7958	148.6	1.4395	51.2	1.5	47.3	0.87	0.04	0.83
	-3	0.8088	225.9	1.4478	66.4	0.0	33.6	0.90	0.00	0.90
II -2	+11	0.8062	225.0	1.4351	93.7	0.0	6.3	0.17	0.00	0.17
	-3	0.7742	218.4	1.4345	93.5	0.0	6.5	0.17	0.00	0.17
III -2	-70	0.8209	218.4	1.4530	58.6	0.0	41.4	1.12	0.00	1.12
	-4	0.8286	228.0	1.4566	57.0	0.0	43.0	1.26	0.00	1.26
IV -1	-70	0.8101	152.0	1.4429	37.8	0.0	62.2	1.20	0.00	1.20
	-3	0.8065	229.0	1.4481	71.1	0.0	28.9	0.79	0.00	0.79
V -1	-70	0.7948	148.0	1.4400	48.9	0.0	51.1	0.89	0.01	0.88
	-2	0.8266	222.0	1.4554	56.1	0.0	43.8	1.25	0.00	1.25
	-3	0.8285	223.9	1.4561	56.5	0.0	43.5	1.25	0.00	1.25
	-4	0.8331	228.5	1.5482	55.2	0.0	44.8	1.34	0.00	1.34
VI -1	-60	0.9008	150.9	1.5177	39.3	57.9	2.8	1.28	1.23	0.03
	-3	0.9093	216.9	1.5133	43.1	40.4	16.5	1.76	1.26	0.50
	-4	0.9137	231.5	1.5088	34.2	23.7	42.1	2.28	0.82	1.46
VII -2	-60	0.9689	176.5	1.5626	37.7	52.0	10.3	2.06	1.72	0.34
	-3	0.9632	182.5	1.5472	21.4	53.4	25.2	2.20	1.50	0.70
	-4	0.9856	199.4	1.5592	17.8	52.6	29.6	2.58	1.63	0.93

Table 3. The acoustic properties of individual hydrocarbons at 20 °C

No.	Product	$M \times 10^3$ [kg]	$\rho \times 10^3$ [kgm ⁻³]	c [ms ⁻¹]	$\beta_s \times 10^8$ [m ² kg ⁻¹]	R [m ^{10/3} s ^{-1/3}]	$\frac{W}{[kG^{1/7}m^{20/7}]}$ [s ^{2/7}]	$J \times 10^{10}$ [m]	$d_n^* \times 10^{10}$ [m]	$d_{ref}^* \times 10^{10}$ [m]	References
1	n-hexane	86.17	0.654	1083	1.322	1371.05	344.39	0.7105	5.39	4.56	[1]
2	n-heptane	100.20	0.684	1162	1.083	1540.09	388.55	0.6431	5.60	4.79	[1]
3	n-octane	114.22	0.704	1193	0.998	1720.74	435.37	0.6174	5.80	5.01	[2]
4	n-nonane	128.25	0.738	1248	0.870	1870.99	475.57	0.5764	5.99	5.20	[1]
5	n-decane	144.62	0.730	1253	0.873	2135.78	541.92	0.5777	6.16	5.73	[18]
6	n-dodecane	170.15	0.749	1297	0.794	2477.40	629.88	0.5506	6.50	5.67	[18]
7	n-tridecane	182.21	—	—	—	—	—	—	—	5.84	[18]
8	n-tetradecane	198.24	0.763	—	—	—	—	—	6.82	6.00	[18]
9	n-hexadecane	226.27	—	—	—	—	—	—	7.12	6.25	[18]
10	cyclohexane	84.16	0.779	1276	0.738	1171.80	299.84	0.5487	5.08	4.46	[2]
11	methylcyclohexane	—	—	—	—	—	—	—	—	—	[1]
12	hexane	98.18	0.764	1247	0.842	1383.20	353.34	0.5700	—	—	[1]
13	cis-decahydronaphthalene	138.24	0.895	1451	0.531	1748.64	453.62	0.4500	—	—	[2]
14	thylene	138.24	0.873	1403	0.582	1772.71	458.97	0.4713	—	—	[2]
15	hydroindane	118.17	0.910	1403	0.558	1453.73	378.62	0.4618	—	—	[1]
16	tetraline	132.20	0.969	1484	0.469	1556.15	407.86	0.4231	—	—	[2]
17	benzene	78.11	0.878	1326	0.648	977.37	253.91	0.4974	4.80	4.36	[2]
18	toluene	92.13	0.866	1328	0.655	1169.36	303.20	0.5001	5.05	4.62	[2]
19	m-xylene	106.16	0.863	1340	0.645	1356.18	351.31	0.4965	5.30	4.85	[1]
20	ethylbenzene	106.16	0.868	1334	0.644	1347.70	349.43	0.4957	5.32	4.85	[2]
21	1,3,5-trimethylbenzene	120.19	0.863	1362	0.625	1543.77	399.60	0.4884	5.66	5.08	[2]
22	hybenzene	120.19	0.894	1372	0.594	1493.88	388.50	0.4764	—	—	[18]
23	iso-propylbenzene	120.19	0.862	1342	0.644	1537.96	398.31	0.4960	—	—	[1]
24	pseudobutylm-xylene	162.28	0.868	1354	0.628	2068.97	535.97	0.4899	—	—	[1]
24	diphenylene methane	168.22	1.007	1514	0.433	1918.18	505.03	0.4068	—	—	[2]

* d_n and d_{ref} [17]

VII were separated on silica gel. By complexing fraction I with urea fractions II and III were separated. By complexing fraction III with thiourea fractions IV and V were separated.

The density ρ_4^{20} ($\pm 1 \times 10^{-4}$), the optical refractive index n_D^{20} ($\pm 1 \times 10^{-4}$), and the molecular weight M (1%) of the fractions were measured. The dependence of the density on temperature was calculated according to [14]. The other quantities were determined by standard methods according to the Polish Standards. The carbon content and the number of rings in specific types of structure were determined by the $n - \rho - M$ and $G - L$ methods of structural analysis [3, 18]. The ultrasonic velocity ($\pm 0.5\%$) as a function of temperature at normal pressure $c(T)$ was measured by the ultrasonic interferometric method developed at the Institute of Aviation (in cooperation with the Institute of the Fundamental Technological Research). The quantity $c(T)$ was measured over a temperature range from the solidification point of the fraction to $+80^\circ\text{C}$ at a frequency of 10 MHz. Using the quantities c , ρ , M , the respective values of the quantities defined by relations (1)-(9) were determined.

4. Results

The characteristic ranges of the values of the coefficient of isentropic compressibility at 20°C for the paraffin and naphthene fractions (I-V), and for the aromatic fractions (VI, VII) were respectively $0.63-0.74 \cdot 10^{-3} \text{ m}^2 \cdot \text{kG}^{-1}$ and $0.45-0.57 \cdot 10^{-3} \text{ m}^2 \cdot \text{kG}^{-1}$ (see Table 4). It follows from these results that β_s can be used in structural identification. In the case of the aromatic hydrocarbon fractions, unicyclic structures can be distinguished from polycyclic ones.

The coefficients of correlation and regression (Table 7) showed a linear relation between $c(n)$ and $\beta_s(n)$ on a logarithmic scale, Figs. 1,2, particularly clearly for aromatic fractions.

The functions $R(M)$ and, particularly, $W(M)$ were also found to be linear (see Figs. 3, 4). As before this linearity was better for the aromatic hydrocarbon fractions. For the other fractions the maximum nonlinearity was $\pm 5\%$ (Table 4). This was confirmed by the coincidence of the value of the coefficients of regression (Table 7) and the behaviour of these functions for the individual hydrocarbons. No linear correlation was found for the relation $L(M)$.

The behaviour of the relation $J(T)$ (Fig. 5) and the temperature dependence of the other acoustic quantities (Tables 5, 6) confirmed the structurally varied character of the fractions. The same distinct differentiation of fractions occurs in the case of the relation $\beta_s(J)$ (Fig. 6). The results discussed so far can be used for the structural identification of multi-component hydrocarbon mixtures.

A separate group of results giving information about the molecular structure consists of the quantities describing such statistical parameters of the molecules as the diameters, defined acoustically or from refraction, and the Jacobson

Table 4. The acoustic properties of the fractions at 20 °C

No.	Product	e [ms ⁻¹]	$\Delta c/\Delta T$ [m °C ⁻¹ s ⁻¹]	$\beta_s \times 10^3$ [m ² kG ⁻¹]	R [m ^{10/3} s ^{-1/3}]	W [$\frac{\text{kG}^{1/2} \text{m}^{20/7}}{\text{s}^{2/7}}$]	$J \times 10^{10}$ [m]	L [mkG ^{1/2} s ⁻¹ °C ⁻¹]	$d_a \times 10^{10}$ [m]	$d_{\text{ref}} \times 10^{10}$ [m]	V_M [m/s]
1	I - 2	1303.4	4.12 ⁻²⁰ ₆₀	0.740	2039.74	522.99	0.5315	50.22 ⁻²⁰ ₅₀	6.108	5.382	186.73
2	I - 3	1365.7	—	0.563	3098.80	794.61	0.5032	—	—	6.188	279.30
3	II - 2	1354.1	3.63 ¹⁰ ₄₀	0.676	3087.62	791.70	0.5083	54.40 ¹⁰ ₄₀	6.920	6.136	279.09
4	II - 3	1363.5	—	0.695	3128.13	797.20	0.5151	—	—	6.155	282.10
5	III - 2	1364.1	3.62 ⁻²⁰ ₆₀	0.655	2950.61	758.26	0.5000	53.42 ⁻²⁰	6.861	6.109	266.05
6	III - 4	1380.1	—	0.634	3063.56	787.90	0.4919	—	—	6.192	275.16
7	IV - 1	1328.2	3.96 ⁻²⁰ ₆₀	0.699	2063.01	529.81	0.5166	48.86 ⁻²⁰	6.139	5.403	187.63
8	IV - 3	1363.5	—	0.667	3148.59	807.11	0.5047	—	—	6.224	283.99
9	I - 1	1306.8	4.00 ⁻²⁰ ₆₀	0.737	2035.82	521.83	0.5305	48.68 ⁻²⁰ ₆₀	6.091	5.379	186.21
10	V - 3	1367.5	3.78 ⁻²⁰ ₆₀	0.647	2981.03	766.74	0.4971	56.30 ⁻²⁰	6.865	6.138	268.57
11	V - 3	1371.9	—	0.641	3002.86	722.49	0.4949	—	—	6.153	270.25
12	V - 4	1384.4	—	0.626	3056.87	786.67	0.4891	—	—	6.142	279.28
13	VI - 1	1399.4	3.86 ⁻²⁰ ₆₀	0.567	1873.73	487.36	0.4653	47.46 ⁻²⁰	5.998	5.439	167.52
14	VI - 3	1439.8	—	0.531	2693.52	700.57	0.4501	—	—	6.104	238.53
15	VI - 4	1438.7	—	0.529	2860.25	744.48	0.4494	—	—	6.213	253.36
16	VII - 2	1482.5	3.55 ⁻²⁰ ₆₀	0.470	2077.13	544.42	0.4235	47.16 ⁻²⁰ ₆₀	6.235	5.723	182.16
17	VII - 3	1473.0	—	0.478	2155.83	564.74	0.4275	—	—	5.755	189.77
18	VII - 4	1488.0	—	0.458	2309.72	606.75	0.4183	—	—	5.917	202.31

Table 4. The acoustic properties of the fractions at 20 °C

Table 5. The dependence of the acoustic properties of the fractions of fuel 1 on temperature

No.	Product	T [°C]	$\rho \times 10^3$ [kgm ⁻³]	c [ms ⁻¹]	$\frac{\Delta c}{\Delta T}$ [m ² °C ⁻¹ s ⁻¹]	$\beta_s \times 10^3$ [m ² kg ⁻¹]	E [m ^{10/9} s ^{-1/3}]	W [kg ^{1/7} m ^{20/7} s ^{2/7}]	J × 10 ¹⁰ [m]	L [mkG ^{1/2} s ⁻¹ °C ⁻¹]	d _a × 10 ¹⁰ [m]
1		-20	0.8269	1471.6	—	0.558	2044.07	523.94	—	—	6.071
2		-10	0.8191	1425.2	4.64	0.601	2041.62	523.40	—	55.56	6.038
3		0	0.8114	1384.3	4.09	0.643	2041.08	523.29	0.4716	49.86	6.074
4	I	10	0.8036	1342.5	4.18	0.690	2039.94	523.04	0.5019	50.95	6.066
5		20	0.7958	1303.4	3.91	0.740	2039.74	522.99	0.5315	47.66	6.108
6		30	0.7880	1263.6	3.98	0.795	2038.74	522.77	0.5625	48.52	6.130
7		40	0.7802	1224.5	3.91	0.855	2037.66	522.54	0.5936	47.66	—
8		-20	0.8402	1490.7	—	0.536	2066.61	530.60	—	—	6.080
9		-10	0.8327	1446.6	4.41	0.574	2064.45	530.13	—	54.37	6.041
10		0	0.8251	1496.9	3.97	0.612	2064.23	530.08	0.4601	48.95	6.054
11	IV	10	0.8176	1368.8	3.81	0.653	2064.19	530.07	0.4880	46.97	6.107
12		20	0.8101	1329.2	3.96	0.699	2063.01	529.81	0.5165	48.82	6.139
13		30	0.8026	1289.5	3.97	0.749	2061.35	529.44	0.5462	48.96	6.122
14		40	0.7951	1252.9	3.66	0.801	2060.92	529.35	0.5747	45.12	—
15		-20	0.8259	1471.6	—	0.559	2038.28	522.37	—	—	6.001
16		-10	0.8181	1430.0	4.16	0.598	2038.14	522.34	—	50.61	6.007
17		0	0.8104	1390.6	3.94	0.638	2038.43	522.40	0.4697	47.93	6.090
18	V	10	0.8026	1346.9	4.37	0.687	2036.45	521.97	0.5006	53.16	6.073
19		20	0.7948	1306.8	4.06	0.737	2035.82	521.83	0.5305	48.78	6.091
20		30	0.7870	1267.6	3.92	0.791	2035.23	521.70	0.5611	47.69	6.072
21		40	0.7792	1231.5	3.61	0.846	2035.91	521.85	0.5906	43.92	—
22		-20	0.9261	1555.7	—	0.446	1888.02	490.54	—	—	5.952
23		-10	0.9198	1514.7	4.10	0.474	1884.10	489.67	—	50.36	5.950
24		0	0.9135	1475.8	3.89	0.503	1880.72	488.91	0.4169	47.79	6.004
25	VI	10	0.9071	1333.5	4.23	0.536	1875.71	487.80	0.4424	51.26	5.931
26		20	0.9008	1399.4	3.41	0.567	1873.73	487.36	0.4653	41.89	5.998
27		30	0.8945	1362.2	3.72	0.602	1870.06	486.54	0.4898	45.70	6.028
28		40	0.8881	1323.9	3.83	0.642	1865.72	485.57	0.5146	47.05	—

Table 6. The dependence of the acoustic properties of the fractions of fuel 2 on temperature

No.	Product	T [°C]	$\rho \times 10^3$ [kg m ⁻³]	c [ms ⁻¹]	$\Delta c/\Delta T$ [m ⁻¹ °C ⁻¹ s ⁻¹]	$\beta_s \times 10$ [m ² kg ⁻¹]	R [m ¹⁰ /s ^{-1/3}]	$\frac{W}{s^{2/7}}$ [kg ^{1/7} m ^{20/7} s ^{-2/7}]	J × 10 ¹⁰ [m]	L [mkG ^{1/2} s ⁻¹⁰ C]	$d_a \times 10^{10}$ [m]
1		10	0.8138	1390.3	—	0.636	3085.80	791.30	0.4857	—	6.883
2	II - 2	20	0.8062	1354.1	3.62	0.676	3087.62	791.70	0.5083	54.30	6.920
3		30	0.7985	1317.3	3.68	0.722	3088.89	791.90	0.5360	55.20	6.945
4		40	0.7909	1281.5	3.58	0.770	3090.06	792.24	0.5633	53.70	—
5		-20	0.8504	1508.0	—	0.517	2945.08	757.04	—	—	6.734
6		-10	0.8430	1470.5	3.75	0.549	2946.09	757.26	—	55.42	6.670
7		0	0.8357	1438.0	3.25	0.579	2949.77	758.07	0.4473	48.03	6.793
8	III - 2	10	0.8282	1400.1	3.79	0.616	2950.10	758.15	0.4740	56.01	6.808
9		20	0.8209	1364.1	3.60	0.655	2950.61	758.26	0.5000	53.20	6.861
10		30	0.8135	1326.5	3.76	0.699	2949.83	758.09	0.5274	55.57	6.853
11		40	0.8061	1291.1	3.54	0.744	2950.19	758.17	0.5538	52.32	—
12		-20	0.8561	1522.0	—	0.504	2982.86	767.15	—	—	6.750
13		-10	0.8487	1484.7	3.73	0.535	2984.09	767.42	—	55.58	6.840
14		0	0.8414	1444.6	4.01	0.570	2982.63	767.10	0.4437	59.75	6.838
15	V - 2	10	0.8340	1406.0	3.86	0.607	2982.05	767.00	0.4704	57.51	6.867
16		20	0.8266	1367.5	3.90	0.647	2980.67	766.66	0.4972	58.11	6.865
17		30	0.8192	1331.0	3.60	0.689	2980.96	766.73	0.5238	53.64	6.883
18		40	0.8118	1295.3	3.57	0.734	2980.99	766.74	0.5501	53.19	—
19		-20	0.9911	1624.0	—	0.383	2093.26	548.04	—	—	6.147
20		-10	0.9855	1587.3	3.67	0.403	2089.17	547.12	—	48.76	6.144
21		0	0.9800	1552.0	3.44	0.423	2085.61	546.32	0.3825	45.70	6.162
22	VII - 2	10	0.9744	1518.9	3.49	0.445	2105.35	551.64	0.4031	46.63	6.198
23		20	0.9689	1482.5	3.55	0.470	2100.67	550.59	0.4235	47.43	6.225
24		30	0.9634	1446.5	3.60	0.496	2095.42	549.41	0.4444	48.10	6.230
25		40	0.9578	1411.0	3.55	0.524	2090.29	548.25	0.4649	47.43	—

Table 7. The coefficients of correlation and regression for the dependencies analyzed

Dependence	Correlation coefficient r	Coefficients of regression equations		
		a	b	c
paraffin and naphthene fractions				
$\beta_s(n)$	-0.799	—	—	—
$\beta_s(n)$	0.808	9284.86	-11055.2	3715.04
$\log \beta_s(n)$	-0.795	4.9648	-2.1694	—
$\log \beta_s(\log n)$	-0.796	2.9801	-7.1954	—
$c(n)$	0.854	9223.64	-13306.7	5435.83
$R(M)$	0.989	230.47	12.546	—
$W(M)$	0.993	135.62	8.7459	—
aromatic fractions*				
$\beta_s(n)$	-0.910	393.01	-222.62	—
$\beta_s(n)$	0.944	6486.69	-8210.97	2617.43
$\log \beta_s(\log n)$	-0.929	2.8772	-6.2770	—
$c(n)$	0.927	-38600.6	50688.0	-16023.6
$R(M)$	0.923	445.68	9.0799	—
$W(M)$	0.951	196.29	7.2590	—

* Data on the aromatic fractions of other fuels [16] were also used in the calculation of the coefficients.

constants, which are a measure of the intermolecular distances. They form a group of the same quantities at, for example, the density, the optical refractive index, the molecular weight, etc. which, in the case of mixtures, must be regarded as mean values. In the case of the dependence $d_{\text{ref}}(M)$, a higher concentration of results occurs both for the fractions and for the individual hydrocarbons, than for $d_a(M)$ (Figs. 7, 8). It follows from this that the diameter determined from refraction is better related to the molecular mass. The larger interval of values of d_a corresponding to a given range of M indicates, in turn, the higher "precision" of the acoustic measurements. The relations between c , β_s , J and V_M are a complementary system (Figs. 2, 6, 9-11). The intermolecular distance decreases with increasing M , while the ultrasonic wave velocity and the coefficient of compressibility increase. Likewise, increasing J causes c to decrease and β_s to increase (Fig. 6).

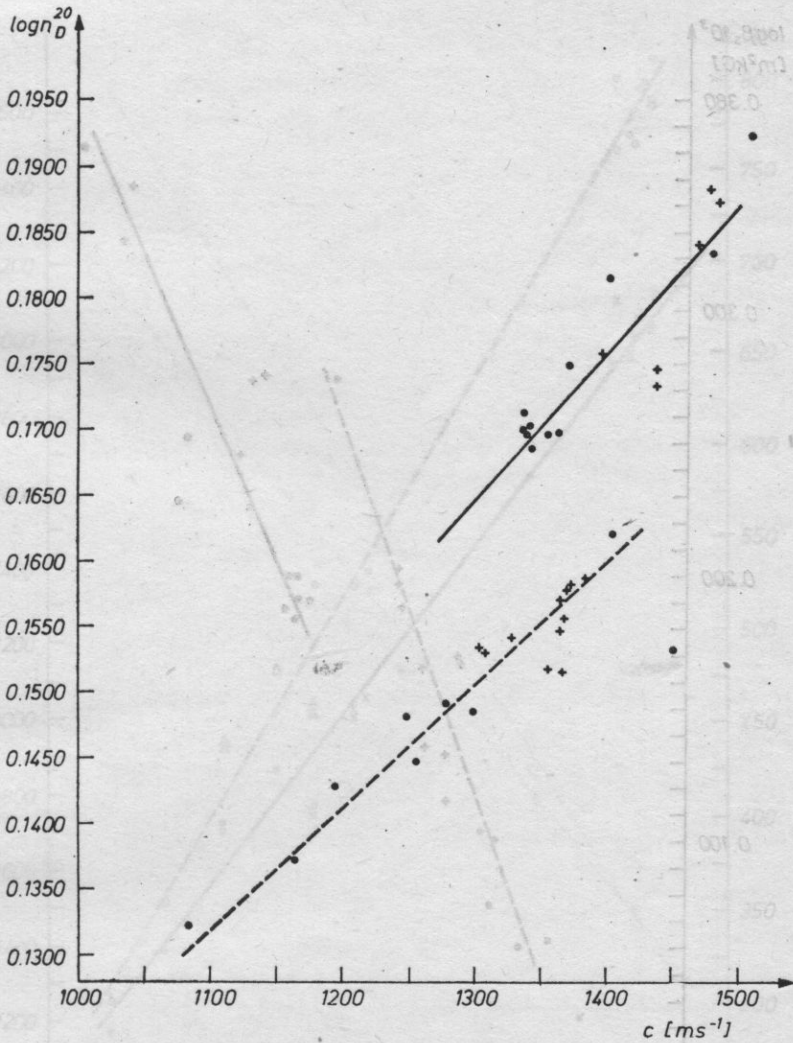


Fig. 1. The dependence of the optical refractive index on the ultrasonic velocity: paraffin and naphthene hydrocarbons — — —, aromatic hydrocarbons — — —, fractions x, individual. ●

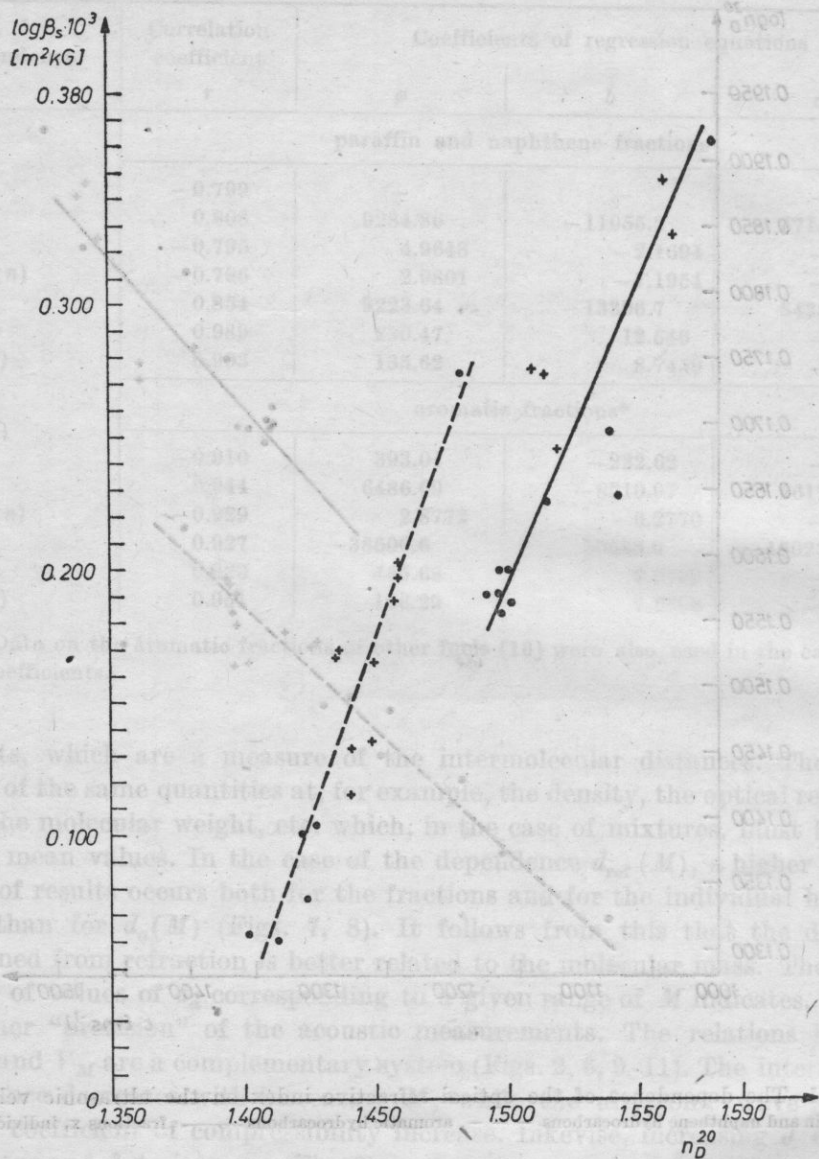


Fig. 2. The dependence of the coefficient of compressibility on the optical refractive index symbols as in Fig. 1

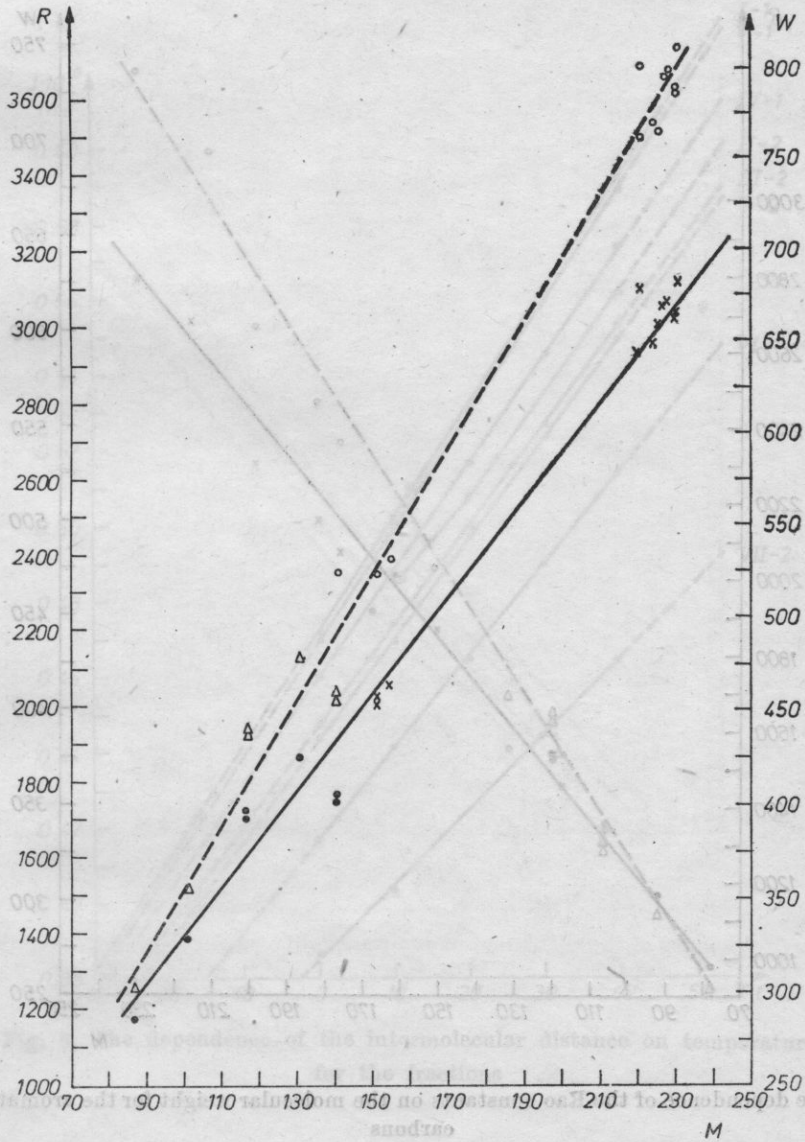


Fig. 3. The dependence of the Rao constants on the molecular weight for paraffin and naphthene hydrocarbons

$R(M)$ ———, fractions x , individual \bullet ; $W(M)$ - - -, fractions o , individual \circ

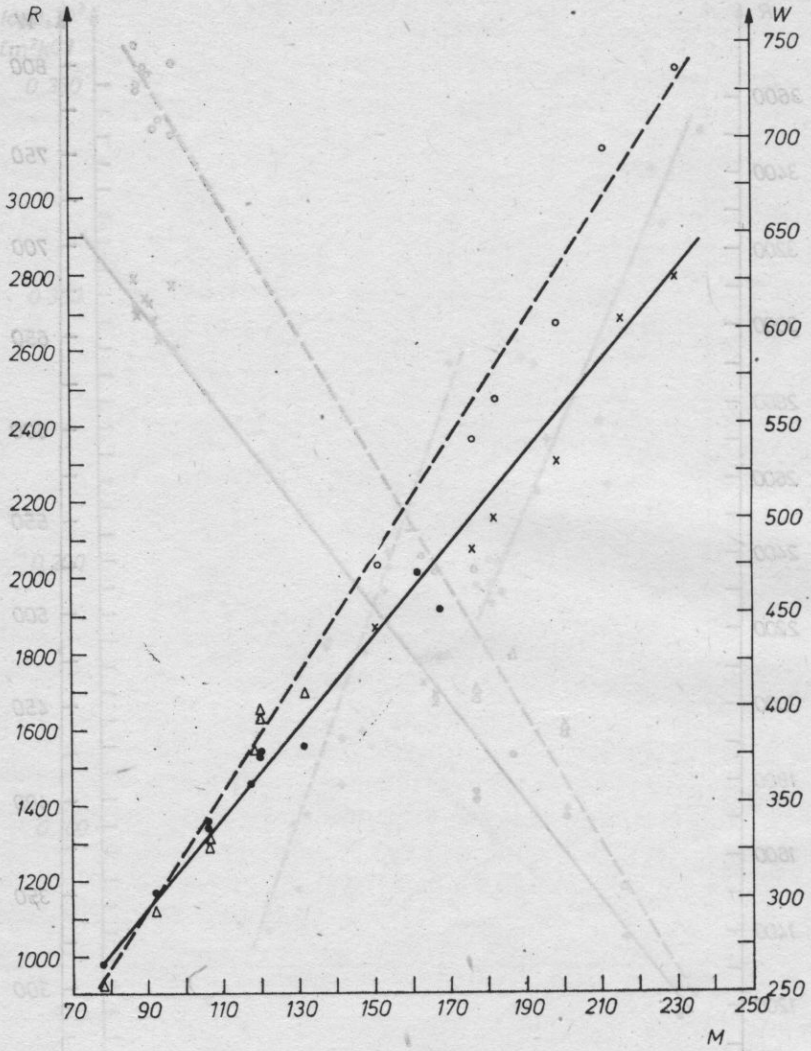


Fig. 4. The dependence of the Rao constants on the molecular weight for the aromatic hydrocarbons symbols as in Fig. 3

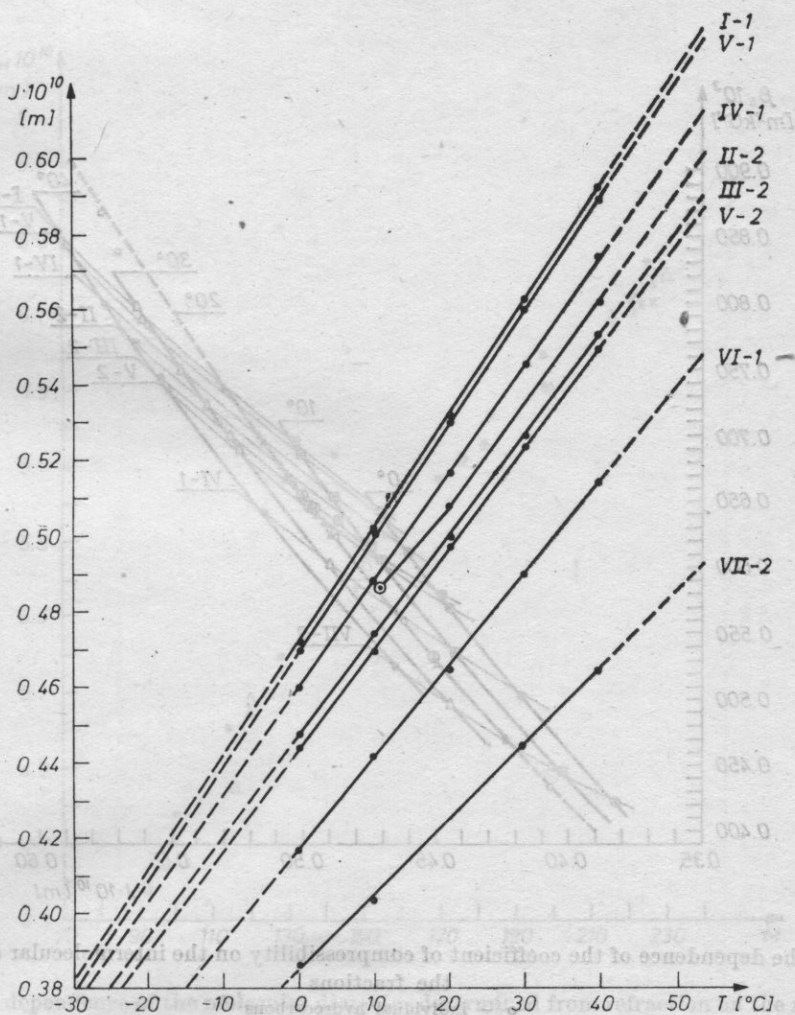


Fig. 5. The dependence of the intermolecular distance on temperature for the fractions

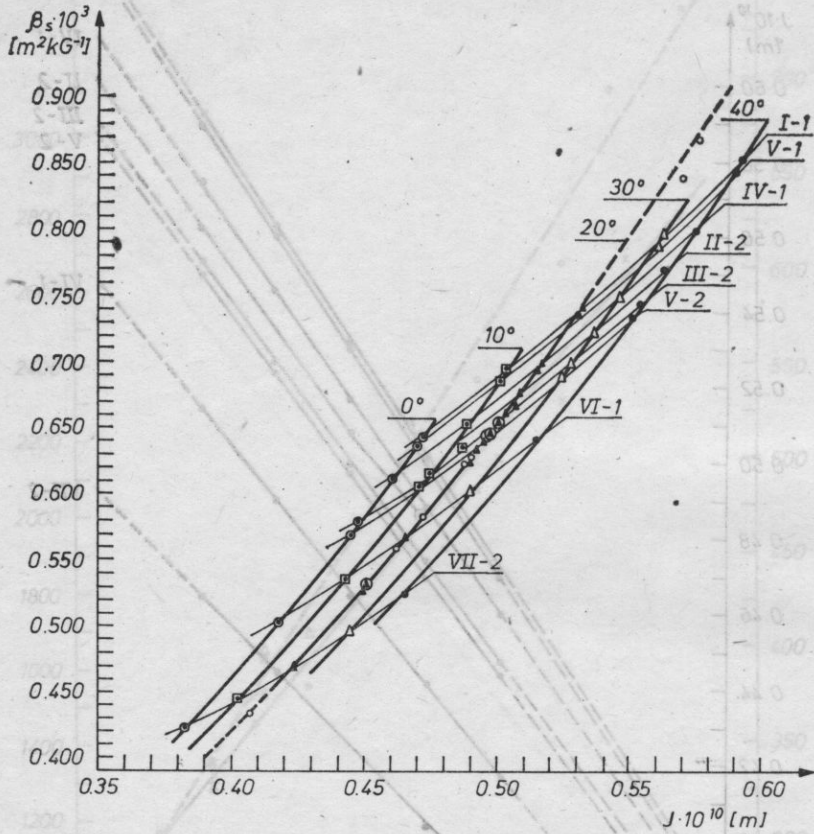


Fig. 6. The dependence of the coefficient of compressibility on the intermolecular distance for the fractions

o - individual hydrocarbons

Fig. 5. The dependence of the intermolecular distance on temperature for the fractions

Fig. 4. The dependence of the Rao constants on the molecular weight for the aromatic hydrocarbons

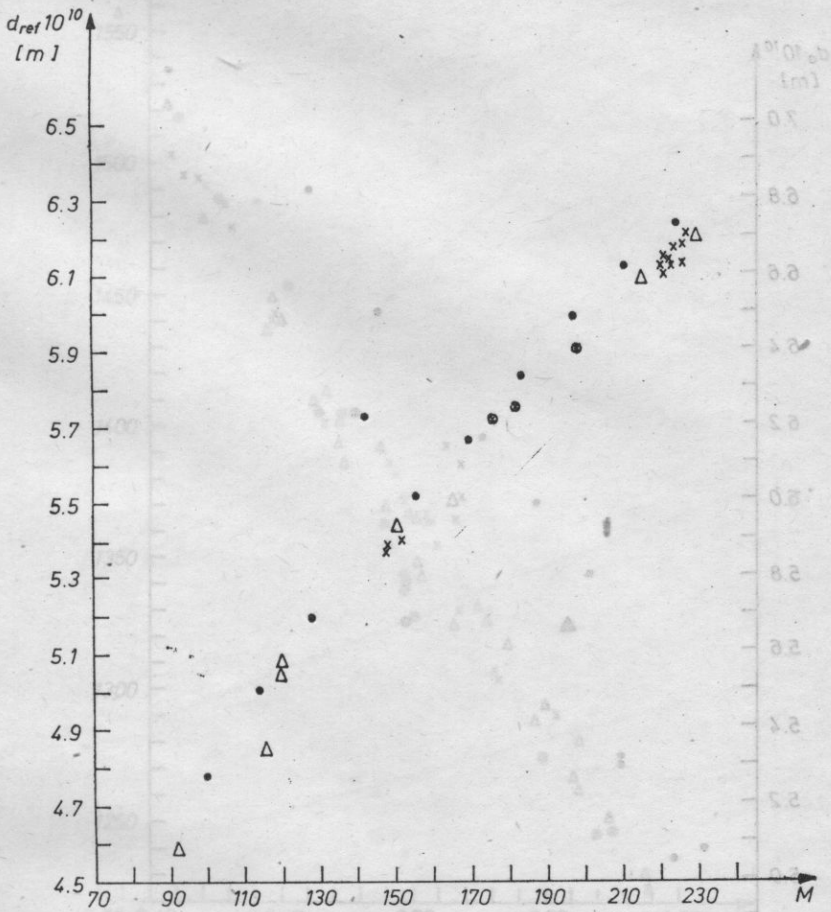


Fig. 7. The dependence of the molecular diameter determined from refraction on the molecular weight
 paraffin and naphthene fractions x; fractions of aromatic hydrocarbons: unicyclic Δ , polycyclic x, individual hydrocarbons \bullet

Fig. 8. The dependence of the molecular diameter determined acoustically on the molecular weight
 symbols as in Fig. 7

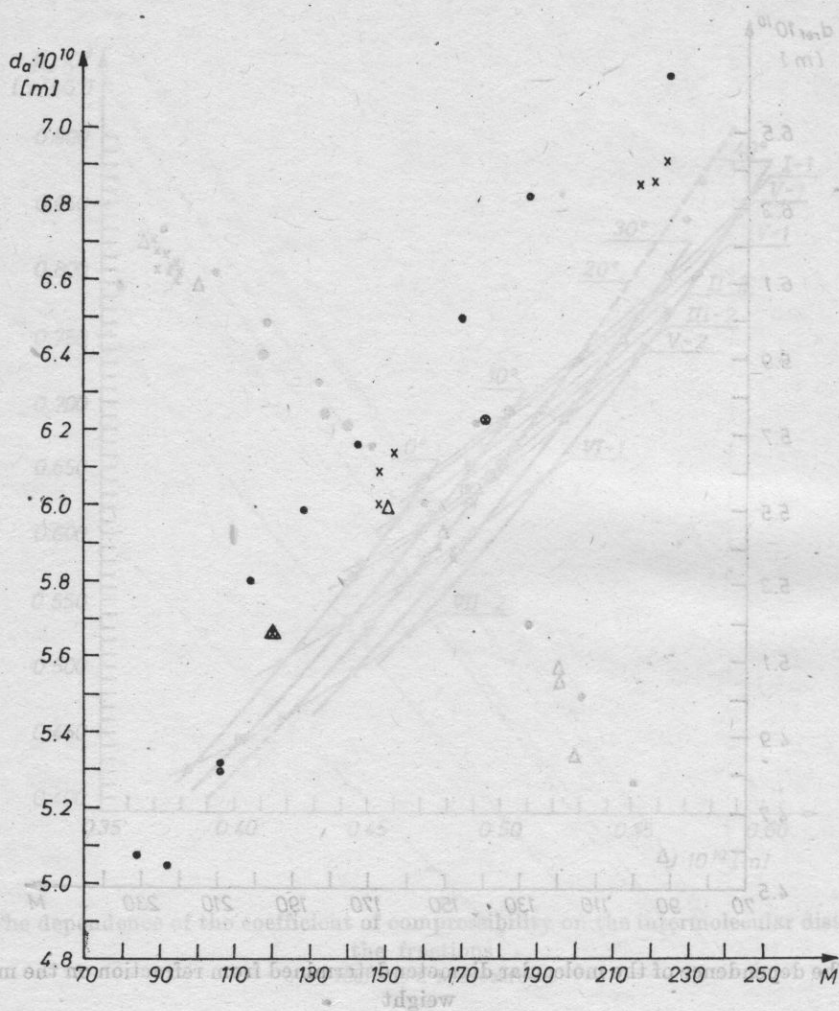


Fig. 8. The dependence of the molecular diameter determined acoustically on the molecular weight symbols as in Fig. 7

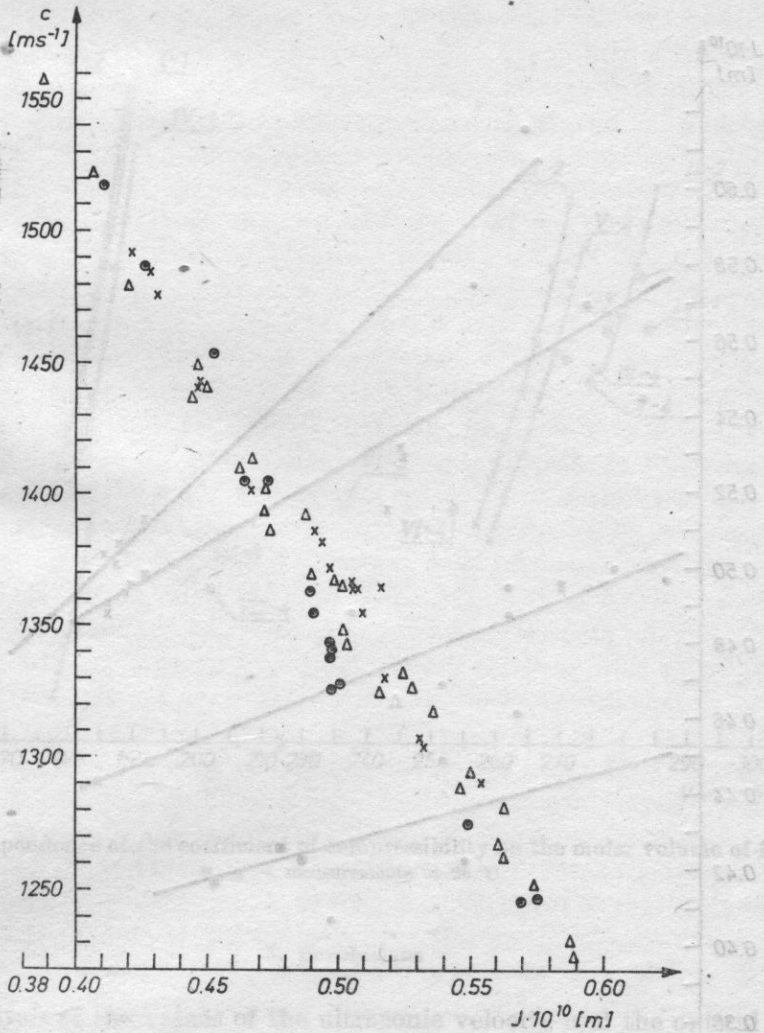


Fig. 9. The dependence of the ultrasonic velocity on the intermolecular distance for fractions and individual hydrocarbons at 20 °C, x and ⊙, and for fractions at other temperatures Δ

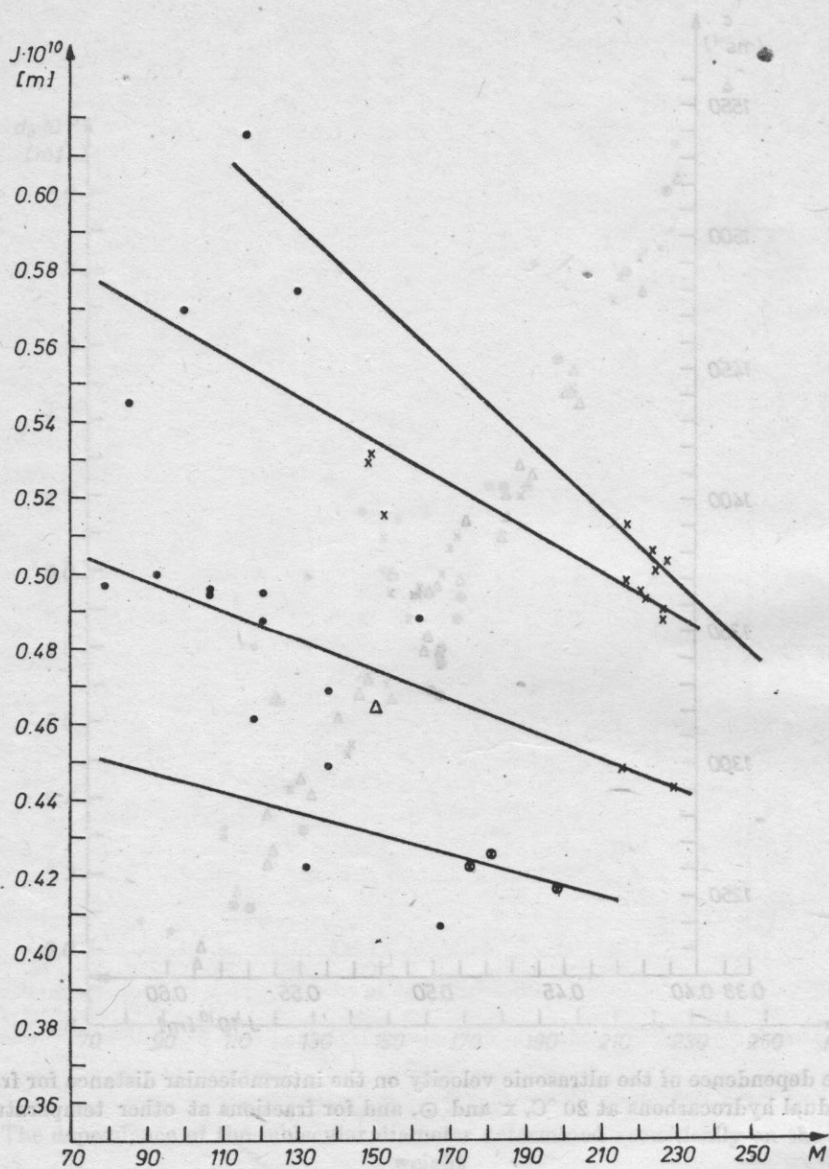


Fig. 10. The dependence of the intermolecular distances at 20 °C on the molecular weight symbols as in Fig. 7

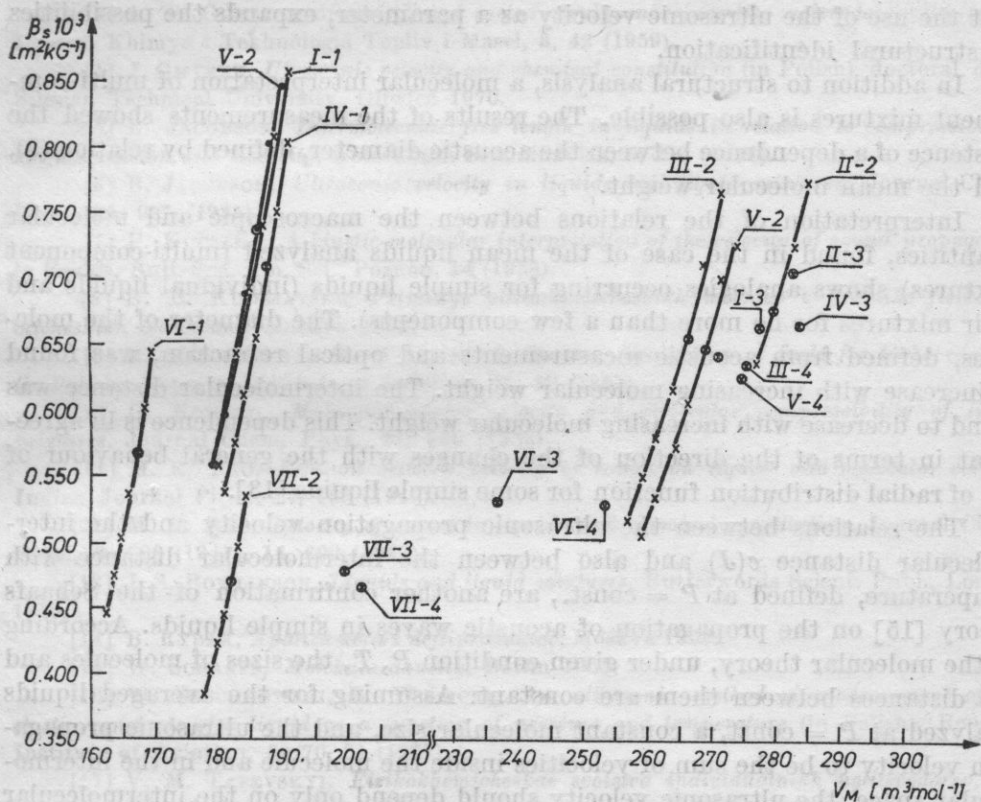


Fig. 11. The dependence of the coefficient of compressibility on the molar volume of fractions
 ●, x — measurements at 20°C

5. Conclusions

The analysis of the values of the ultrasonic velocity and the optical refractive index for saturated individual hydrocarbons and their complex mixtures permits the following analogies to be stated; a distinct change in the value of c and n can be observed with an increase in the number of carbons in the molecules and with the density, and in the transition from paraffin or naphthene structures to aromatic structures, unicyclic and polycyclic, in condensed systems, particularly in the latter case.

The results of the investigations of the fractions showed the validity of the Rao rules to extend to complex multi-component mixtures. Extrapolation permits the use of these quantities for identifying the type of the basic structure of mixtures of unknown content. This applies both to hydrocarbon mixtures of different structural types, and to the introduction into molecules of a given structural type of other structures, e.g. paraffin chains into a benzene ring. Changes in the value of R and W should be expected in both cases. It follows

that the use of the ultrasonic velocity as a parameter, expands the possibilities of structural identification.

In addition to structural analysis, a molecular interpretation of multi-component mixtures is also possible. The results of the measurements showed the existence of a dependence between the acoustic diameter, defined by relation (8), and the mean molecular weight.

Interpretation of the relations between the macroscopic and molecular quantities, found in the case of the mean liquids analyzed (multi-component mixtures) shows analogies occurring for simple liquids (individual liquids and their mixtures for no more than a few components). The diameter of the molecules, defined from acoustic measurements and optical refraction, was found to increase with increasing molecular weight. The intermolecular distance was found to decrease with increasing molecular weight. This dependence is in agreement in terms of the direction of the changes with the general behaviour of the radial distribution function for some simple liquids [13].

The relations between the ultrasonic propagation velocity and the intermolecular distance $c(J)$ and also between the intermolecular distance with temperature, defined at $P = \text{const.}$, are another confirmation of the Schaafs theory [15] on the propagation of acoustic waves in simple liquids. According to the molecular theory, under given condition P, T , the sizes of molecules and the distances between them are constant. Assuming for the averaged liquids analyzed at $P = \text{const.}$, a constant molecular size, and the ultrasonic propagation velocity to be the sum of velocities inside the molecule and in the intermolecular space, the ultrasonic velocity should depend only on the intermolecular distances. This has been confirmed by the results of the investigations.

The analysis of the relations between the macroscopic and molecular quantities also leads to the conclusion that they have distinctly different characters depending on the structural type dominating in the fractions analyzed. This applies to the dependences of the intermolecular distances and the coefficients of compressibility, which are in some manner a measure of these distances, on the temperature, the molecular mass and the molar volume.

It should be noted that in all the cases where the presence of a factor strongly dependent on the interaction of the long-range forces can be expected, the model of a mean liquid can fail, e.g. $\beta_s(M)$. These forces are not sufficiently well accounted for by intermolecular distances, and even less by molecular sizes. The use of a larger variety of narrower and more monostructural fractions would probably be more relevant to these qualifications.

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