RECENT RESULTS IN THE CONTRACTION DETERMINATION OF PETROLEUM PARAFFINS*

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The rating of petroleum paraffins has made great progress in recent years. Producers and users nowadays are not satisfied any more with the knowledge of melting point, oil content, and other conventional characteristics. Spurred on principally by the demand of users, the scope of testing has been significantly extended [1]. One among the newer methods is to determine the contraction of paraffins.

From a point of view of application contraction is a very important phenomenon, obviously because for most of the fields of application, besides chemical stability, physical and functional characteristics of the paraffins play a decisive role, these being in turn directly or indirectly related to contraction. Thus a more detailed study of the contraction of paraffins appeared not to be without interest.

The contraction of paraffins is, of course, a specific volume change upon decrease of temperature. For paraffin melts, and for several modifications of the solid phase the thermal-gradient is max. 0.1 per cent by °C. This value however, shows a significant transient increase at solidification, and in the temperature range of structural transformations in the solid phase peculiar to macrocrystalline paraffins.

According to X-ray diffraction pictures, depending on its average molecular weight solidifying, petroleum paraffin assumes a hexagonal (α) or orthorhombic (β) crystal structure. Phase ratios are shown in Fig. 1. Accordingly carbon atom numbers below and above 37, produce α and β-modifications, respectively, during solidification [2, 3]. Also the hexagonal structure is seen to be stable only in a rather narrow temperature range, even more restricted with the increase of molecular weight. Below this temperature range the α-modification is converted into β-modification. At room temperature, both macrocrystalline paraffins and ceresins exhibit orthorhombic crystalline structures. The α-modification is softer and less dense. In this crystal form the

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long paraffin chains can freely rotate around their longitudinal axis. The β-modification is harder, more dense, and does not allow the rotation of molecules.

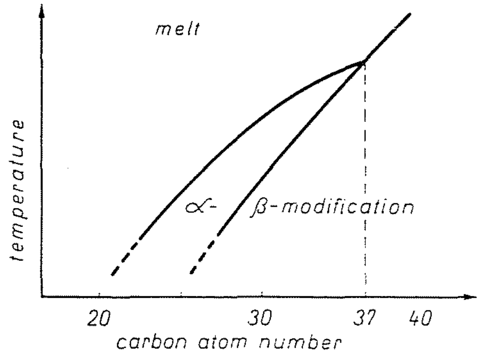

Fig. 1. Phase ratios in paraffins, as function of number of carbon atoms, and of temperature

According to some authors, differential thermoanalysis of solid samples of the normal fractions of petroleum paraffins reveals, above 20 °C, two thermal processes each suggestive of a conversion of modifications, thus suggesting the existence of three modifications [3]. Unfortunately the crystal structure of a third modification has not been elucidated yet by X-ray diffraction analysis.

The most exhaustive structure studies refer to single n-paraffins. Depending on their thermodynamic parameters, the single n-alkanes may assume hexagonal, orthorhombic, triclinal or monoclinal structures [3, 6, 7].

Though distinction is based on other practical criterion [5], let us notice that the average carbon atom number of 37 is the upper limit for macrocrystalline paraffins and lower limit for ceresins.

The aim of our experiments was to determine the contraction between 20° and 80° of some kinds of paraffins and of their fractions separated by adsorption on molecular sieve and silica gel chromatography, with special attention paid to changes of modifications at the point of melting, and the solid phase.

In examining fractions separated by means of molecular sieve to normal and non-normal parts, an attempt was made also to find a possibility to demonstrate by refractometry and eventual second modification change of the solid phase of the normal part of petroleum paraffins. The studies of the fractions separated on silica gel, on the other hand, were aimed at contributing to the knowledge of the specific crystallisation characteristic of ceresins.

Impact of paraffin contraction on the knowledge of functional characteristics

Significant differences of the functional properties of macrocrystalline paraffins and ceresins are known in the practice. Ceresins are much more flexible, less permeable to water vapour, etc.*

These differences may be explained by contraction behaviours in the solid phase as follows.

The principal cause of the rigidity of macrocrystalline paraffins is the stress developing at the temperature of application. This inner stress is due to significant differential contraction during transformation, upon differences of specific volumes.**The higher the stress, the quicker is the transformation i.e., the narrower it's temperature range, or what is equivalent to this, the higher the temperature gradient of the transformation. While transformation occurs practically at one point of temperature in the case of single n-paraffins, in that of commercial paraffins to be considered as mixtures of various chain length hydrocarbons, transformation proceeds over a range of 5 to 10 °C depending on the range of the number of carbon atoms in the various chains. In the former case the gradient of contraction is steep, in the latter much less so but still several times steeper than the gradient found for pure hexagonal or pure orthorhombic modifications.

No allotropic transformation occurs in ceresins of solid state; thus, no contraction due to such transformation occurs and, consequently, structural stresses impairing the functional properties of ceresins are not developed either.

Of course, occurrence or non-occurrence of a change of modifications in the solid state alone does not explain the differences between functional properties of macrocrystalline paraffins and of ceresins. Else, the behaviour of n-paraffins with 37 carbon atoms and over would be similar to that of ceresins.

No published evidence is known, however, to state of the flexibility of, e.g. high molecular weight paraffins to be as good as that of ceresins with the same average molecular weight. The difference is due in part, to the sterical features, different from those of n-alkanes, that are proper to the majority of molecules constituting the ceresins. At congelation, the branches and rings of the ceresin molecules hinder smooth crystallization. A characteristic microcrystalline structure results, which also contributes to better flexibility, etc. Accordingly, development of essential functional characteristics of paraffins is affected by complex effects.

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* These properties are of importance in the manufacture of paraffin impregnated papers for use as packing materials in the food industry.

** This is not the case with contractions during solidification. Then — since one of the phases is a liquid — no inner stresses arise.

Here we might mention that the lustrous surface emerging at the congelation of a macrocrystalline paraffin will loose its gloss at lower temperatures because of structural changes.

The importance of the refractometric method to be discussed resides therein that the shapes of refraction versus temperature curves are illustrative of the process of crystallization and modification changes. A study of the graphs allows to determine the temperature range of congelation, of structural interconversions, and of concomitant contraction or contraction gradients. On this basis a correlation can be established between refraction vs. temperature curves and functional properties of paraffins. Since in general a rather involved process is needed to determine functional properties important for paraffin users, such a correlation would be promising both to producers and users of paraffins, permitting more involved methods to be replaced by simple refractometry tests.

Determination of contraction

Dilatometry serves [8] the direct determination of the contraction of paraffins. However, this method is quite complicated and involves several sources of error. Refractometry, though an indirect method, is more advantageous since it is rapid, reproducible, and accurate. The principle of the contraction determination by refractometry is derived from the following considerations.

Contraction is a ratio of the change in volume to the initial volume

$$K = 100\frac{v_1 - v_2}{v_1} \tag{1}$$

where K = contraction, v_1 = specific volume at initial temperature, and v_2 = specific volume at final temperature.

On the basis of the Lorenz—Lorentz formula [9, 10] known in physical optics

$$r_L = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} \tag{2}$$

where r_L = specific refraction, n = index of refraction, and d = density.

Since in practical calculations, specific refraction is a constant unaffected by temperature, further, since density and specific volume are reciprocals to each other, Eqs (1) and (2) give

$$\frac{d_1}{d_2} = \frac{n_1^2 - 1}{n_1^2 + 2} \cdot \frac{n_2^2 + 2}{n_2^2 - 1} \tag{3}$$

where n_1 and d_1, represent refractive indices and densities, respectively, at initial temperature, and n_2 and d_2 are the same at final temperature.

Using Eq. (3), Eq. (1) can be written as:

$$K = 100\left[1 - \frac{n_2^2+2}{n_2^2-1}\,\frac{n_1^2-1}{n_1^2+2}\right] \tag{4}$$

This means that for the calculation of the contraction in a given range of temperature, only the refractive indices at initial and final temperatures are needed. However, when using Eq. (4), the fact must be kept in mind that, owing to the double refraction of paraffin crystals, two refractive indices arise. Since paraffin belongs to the optically positive crystals the higher value of the refractive index characterizes the extraordinary (n_e) ray and the lower value (n_0) the ordinary ray [10]. These two indices can, in practical calculations be replaced by a mean value weighted with a bias towards the ordinary ray [11].

$$n = \frac{1}{3}(2n_0 + n_e) \tag{5}$$

Thus, in determining the contraction of molten and of solid paraffins, refractive indices as measured and calculated from the measured values, according to Eq. (5) respectively are to be used.

Of course, in thermostated refractometers the refractive index of paraffins either in the liquid or in the solid state can be measured. In the latter case one may proceed by placing the molten sample between the prisms of the refractometer and cooling it to congeal, into a thin translucent layer. Both refractive indices of paraffins can be read.

Test samples

Gatch, or petrolatum, obtained by solvent extraction of residual oils produced in the separation of bitumen from goudrons, and of paraffinic light and medium cuts from distillations under reduced pressure of Romaskino crudes, all from the refineries of Dunai Kőolajipari Vállalat, were used as starting substances. The samples were won by sweating the paraffin gatch, or through removal of oil by solvent extraction from petrolatum, under laboratory conditions. In what follows, the macrocrystalline paraffin sample obtained from light oil is marked 1, the sample obtained from medium oil is marked 2, and the ceresin sample is marked 3. The more important physical and chemical characteristics of these three samples are shown in Table 1 [12].

Table 1

Principal characteristics of the paraffin samples

		Macrocrystalline paraffins from		Microcrystalline paraffins from residual oil
		light oil	medium oil	
No. of sample		1	2	3
Melting point, °C		52.5	58.0	70–75
Refractive index, n_D^{80}		1.4265	1.4295	1.4410
Oil content per cent by weight		0.33	0.40	3.48
Density, d_4^{80}		0.7701	0.7800	0.8558
Hydrocarbon content, per cent by weight	n-paraffins	90.60	82.70	21.7
	aromatics	0.84	1.43	10.45
	iso-paraffins + naphthenes	8.56	15.87	67.85
Average molecular weight		355	390	570

From samples 1, 2 and 3, normal paraffin samples n1, n2 and n3, and non-normal paraffin samples i1, i2 and i3 were separated on molecular sieves. The carbon atom number distribution of the normal fractions of macrocrystalline paraffin is shown in Fig. 2.* Characteristics of fractions separated on molecular sieves are listed in Table 2.

Under properly chosen experimental conditions of column chromatography with silica gel, non-aromatic fractions can be eluted from samples 1 2 and 3 with reagent gasoline as the first solvent, and aromatic fractions with aromatic free chloroform-ethanol mixture as the second solvent [12]. As shown in Tables 3 and 4, in contrast to the gasoline fractions of macrocrystal-

Table 2

Principal characteristics of paraffin fractions separated on molecular sieves

	Fractions of paraffin samples					
	affected by			unaffected by		
	molecular sieving					
Sample	n1	n2	n3	i1	i2	i3
Yield, per cent by weight	90.6	82.7	21.7	9.4	17.3	78.3
Melting point, °C	32.5	61.0	79.0	40.0	46.0	71.0
Refractive index, n_D^{80}	1.4256	1.4283	1.4419	1.4320	1.4340	1.4390
Average molecular weight	353	392	605	375	396	550

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* Data obtained by gas chromatography in a PYE instrument with flame ionization detector, at 250—270° working temperature.

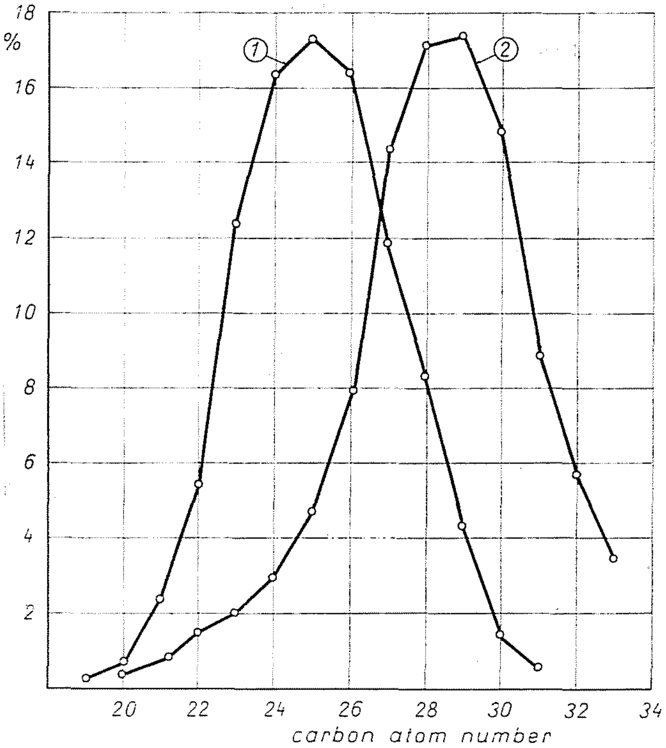

Fig. 2. Distribution, according to the number of carbon atoms, of the n-paraffin content of Samples 1 and 2

Table 3

Some characteristics of the main benzene fractions of macrocrystalline paraffins

Sample No.	Fraction	Characteristics Refraction, n_D^{80}	Melting point, °C	Average molecular weight	Yield, %
1	1—1	1.4265	52.0	355	39.4
	1—2	1.4265	52.0	355	34.8
	1—3	1.4265	52.0	355	16.4
	1—4	1.4265	52.0	355	6.7
2	2—1				0.6
	2—2				0.7
	2—3	1.4300	57.5	392	64.8
	2—4	1.4300	57.5	392	23.7
	2—5	1.4300	57.5	392	6.7
	2—6	1.4300	57.5	392	0.9

Table 4

Some characteristics of the main benzene fractions of ceresins

Sample No.	Fraction	Characteristics			
		Index of refraction, n_D^{80}	Melting point, °C	Average molecular weight	Yield, %
3	3—3	1.4402	64.5	507	22.7
	3—4	1.4405	66.0	510	10.7
	3—5	1.4406	67.5	515	8.0
	3—6	1.4408	68.5	525	5.5
	3—7	1.4410	69.2	536	4.3
	3—8	1.4435	69.2	558	6.1
	3—9	1.4445	71.0	580	4.3
	3—10	1.4502	73.0	658	7.5

line paraffins, the main parts of the fractions eluted from ceresin with gasoline exhibit significant deviations in their refractive indices, solidification points, and molecular weights. This suggested a more thorough study of the gasoline fractions of ceresin, in the course of which the curves of refractive indices against temperature were plotted for gasoline fractions 3—2 to 3—18, and the same curve for the aromatic fraction 3—24; and the contraction of fractions 3 —2 to 3 —10 was calculated, these fractions forming the main part of the non-aromatic ones.

Results and evaluation

Our studies involved the temperature range 20 °C to 80 °C. An Abbe-type refractometer was used. It was found practical to start measurements at 80 °C and proceed by lowering the temperatures. Discontinuities, or sudden changes of direction, in the curves plotted are satisfactory indications of congealing or change of modification. Careful analysis of the curves suggests that, for a determination of contractions due to congealing and to change of modification, the range of temperature should be subdivided into smaller sections, viz. from 80 °C to congealing point, from congealing point to the inception of the change of modification, the domain of the change of modification, from the completion of the change of modification to 20 °C.

Refraction vs. temperature curves of samples 1, 2 and 3, and of their fractions separated on molecular sieves, are shown in Figs 3, 4 and 5; these curves for the fractions of sample 3 separated on silica gel are shown in Fig. 6. The contraction figures calculated according to Eq. (4) from plotted data are compiled in Tables 5 and 6. Analysis of Figures and Tables suggests the following.

Table 5

Contraction of macrocrystalline paraffins and of their fractions separated on molecular sieves

Sample, or fraction	Contraction, % / Temp. range, °C	From 80 °C to congelation	At congelation	From congelation to start of change	Change of modification	From end of change to 20 °C	Overall contraction, 80 °C—20 °C %
1	%	2.14	9.15	0.59	3.11	1.12	16.11
	°C	80—51	51.0	51—41	41—30	30—20	
n1	%	2.41	8.93	0.41	3.17	0.96	15.88
	°C	80—51	51.0	51—40	40—29	29—20	
i1	%	2.85	7.17	1.47			11.49
	°C	80—39	39.0	39		20	
2	%	1.49	9.09	0.71	3.20	1.03	15.52
	°C	80—59	59.0	59—52	52—41	41—20	
n2	%	1.14	9.26	0.78	3.42	1.01	15.61
	°C	80—61	61.0	61—52	52—35	35—20	
i2	%	2.32	7.14	1.66			11.12
	°C	80—73	73.0	73		20	
3	%	0.39	9.78	4.39			14.56
	°C	80—73	73.0	73		20	
n3	%	0.21	7.36	6.85			14.42
	°C	80—79	79.0	79		20	
i3	%	0.60	9.39	4.61			14.60
	°C	80—71	71.0	71		20	

Macrocrystalline paraffins, and their fractions separated on molecular sieves

Figs 3 and 4 show n vs. t curves of samples 1 and 2, and of their fractions separated on molecular sieves. On the left-hand side the $n - t$ curves of the paraffin melts are plotted. In this domain refractive indices change linearly in inverse ratio to temperature. Calculation from data in Table 5 shows that the gradient of contraction is less than 0.1 per cent per centigrade. In both groups the curves pertaining to the parent samples are in the middle, above them are the curves of the fractions unaffected by molecular sieving, and below them the curves of the fractions retained by the molecular sieve. On the right hand side the n vs. t curves of the solid samples of paraffins are shown. The upper and the lower family of curves pertain to the indices referred to the

Table 6

Contraction of Sample 3,
and of its main benzene fractions separated on silica gel

Sample, or fraction	Contraction, % Temp. range, °C	From 80 °C to congelation	At congelation	From congelation to start of change	Change of modification	From end of change to 20 °C	Overall contraction, 80 °C to 20 °C %
3	%	0.39	9.78		4.39		14.56
	°C	80—73	73.0	73.0	—	20	
3—2	%	0.98	4.17	0.10	3.48	3.24	11.97
	°C	80—64	64.0	64—63.5	63.5—57.5	57.5—20	
3—3	%	1.30	7.10	0.57	2.88	2.14	13.99
	°C	80—65	65.0	65—64	64—56	56—20	
3—4	%	0.68	7.60	0.75	2.97	1.66	13.66
	°C	80—66	66.0	66—65.5	65.5—57.5	57.5—20	
3—5	%	0.90	7.64	0.10	3.06	3.08	14.78
	°C	80—67.5	67.5	67.5—66.5	66.5—57.5	57.5—20	
3—6	%	1.03	10.54		2.73		14.30
	°C	80—68	68.0	68.0	—	20	
3—7	%	1.07	9.44		3.86		14.37
	°C	80—69	69.0	69.0	—	20	
3—8	%	0.62	10.18		2.80		13.60
	°C	80—69	69.0	69.0	—	20	
3—9	%	0.87	9.76		3.20		13.83
	°C	80—69	69.0	69	—	20	
3—10	%	1.13	8.78		3.82		13.73
	°C	80—73	73.0	73.0	—	20	

extraordinary and the ordinary ray respectively. These two groups of curves are parallel lines apart by about $\Delta n = 0.05$, thus it is sufficient to analyse the course of one of them. Such an analysis reveals that in the curves pertinent to initial substances, and in those pertinent to fractions affected by molecular sieving, two waves are in evidence. The wave at higher temperatures pertains to the hexagonal modification. Like that of the melts, the contraction gradient of this modification is less than 0.1 per cent per centigrade. This is valid for a temperature range of 10 °C for samples 1 and n1, and 7 °C for samples 2 and n2. This is in agreement with the tendency, evident in Fig. 1, that with the increase of molecular weight the temperature range of the α-phase gets restricted. Cooling of the samples to still lower temperatures brings them into the domain of modification changes. Here the course of $n - t$ curves becomes steep. This is the most important section, from the point of view of internal stresses of paraffins. The greater the change of the refractive index, or of the temperature gradient of contraction, the more important are the internal stresses. Calculated from tabulated data this gradient is about 3 to 4 times that found for the hexagonal modifications.

When the paraffin corresponding to the orthorhombic crystal structure, or its normal fraction, is cooled further to 20 °C, no third wave emerges on the $n - t$ curve. Thus, refractometry does not reveal but one change of modification of petroleum paraffins, and of their normal fractions. Without rejecting outright the existence, suggested by differential thermo-analytical findings, of a third modification, we may conclude that no error in calculations of contraction will be committed by listing under the head of change of modification the interconversion $\alpha \rightleftharpoons \beta$ alone, corresponding to Fig. 1.

Figs 3 and 4 also show that the part of macrocrystalline paraffins unaffected by molecular sieving does not suffer any change of modification. In this respect, these fractions are similar to ceresins, to be discussed later on.

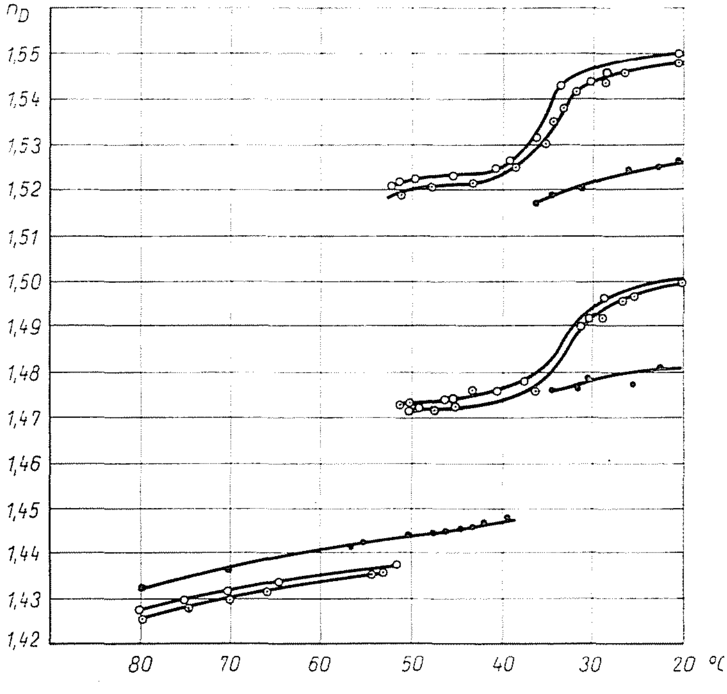

Fig. 3. Refraction vs. temperature curves of Sample 1, and its fraction separated on a molecular sieve. ○ — parent sample, □ — fraction affected by molecular sieving, × — fraction unaffected by molecular sieving

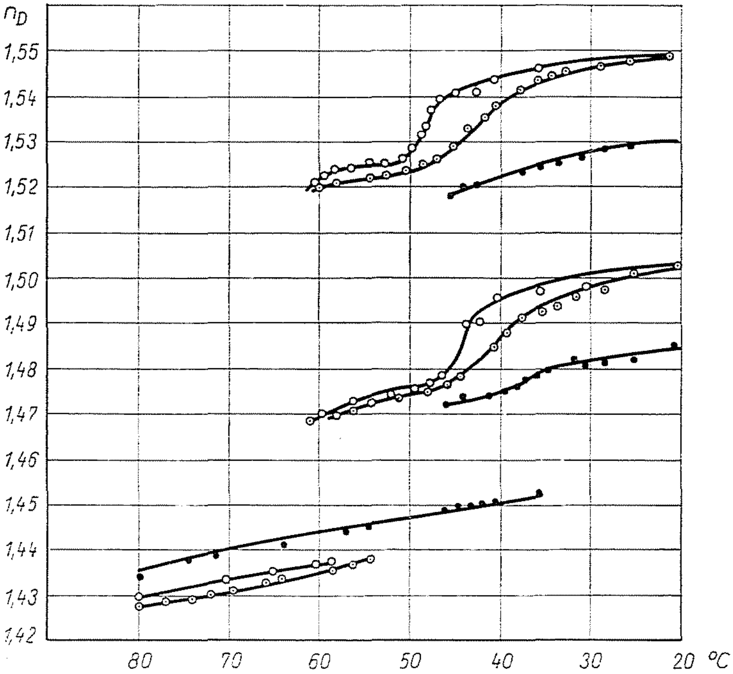

Fig. 4. Refraction vs. temperature curves of Sample 2, and its fractions separated on a molecular sieve. ○ — parent sample, □ — fraction affected by molecular sieving, × — fraction inaffected by molecular sieving

The contraction of macrocrystalline paraffins, and contraction of their fractions affected by molecular sieves, amounts to 15 to 16 per cent between 80 °C and 20 °C. Therefrom about 9 per cent can be ascribed to contraction at solidification, and something above 3 per cent is due to the change of modification. Contraction of fractions unaffected by molecular sieving is less than that of the parent sample, over the entire temperature range, and even at congealing point, and no contraction at all owing to change of modification is in evidence.

Ceresin and its fractions separated on molecular sieves

Fig. 5 shows *n* vs. *t* curves of sample 3, and of its normal, and non-normal fractions. The shape of these curves does not reflect any change of modification either in the parent sample or in its fractions prepared on molecular sieves. Refractive indices of the solid phase samples produce curves with a stronger bend at their start. Based upon correlations between crystal structure and composition, this can be explained as follows.

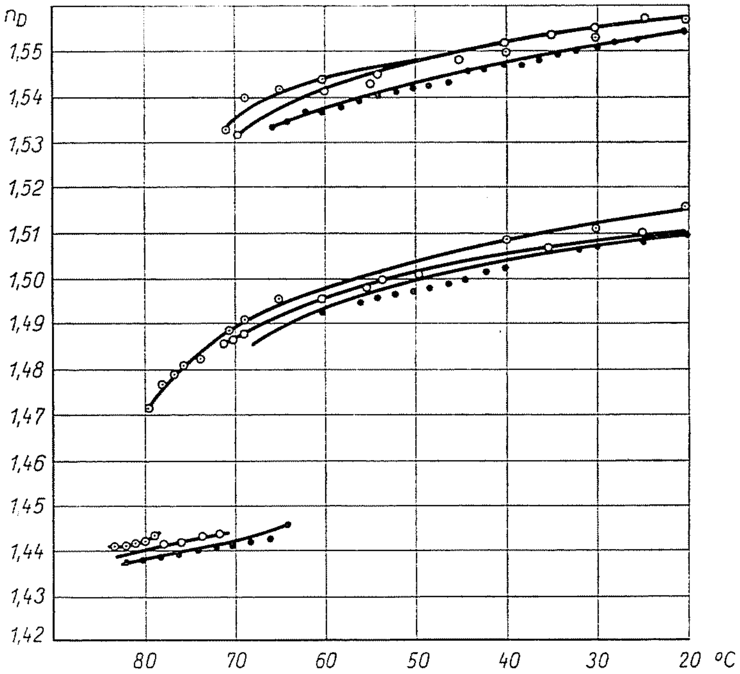

Fig. 5. Refraction vs. temperature curves of Sample 3, and of its fractions separated on a molecular sieve. ○ — parent sample, □ — fraction affected by molecular sieving, × — fraction inaffected by molecular sieving

Change of modification is excluded because the tested ceresin, in agreement with its average molecular weight (570) and average number of carbon atoms (41), assumes the orthorhombic crystal structure just at congelation.

The bend in the refractive index curves of the solid phase samples can be explained by referring to the complicated structure of the ceresin molecules. Owing to steric hindrance, it is only with difficulty, and imperfectly even then, that the long paraffin chains with branchings off and rings can become aligned in closer bundles.

Between 80° and 20 °C, the amount of contraction of ceresin and of its fractions separated on molecular sieves, is about 14 per cent. Of course, no contraction due to change of modification occurs in any of these fractions.

Fractions of ceresin, obtained by chromatography on silica gel

Fig. 6 shows *n* vs. *t* curves of fractions 3 –2 to 3 —18 and 3 —24, obtained by chromatography on silica gel. Table 6 lists the contractions calculated from *n* vs. *t* curves pertaining to fractions 3 –3 to 3—10. A study of these findings suggests the following.

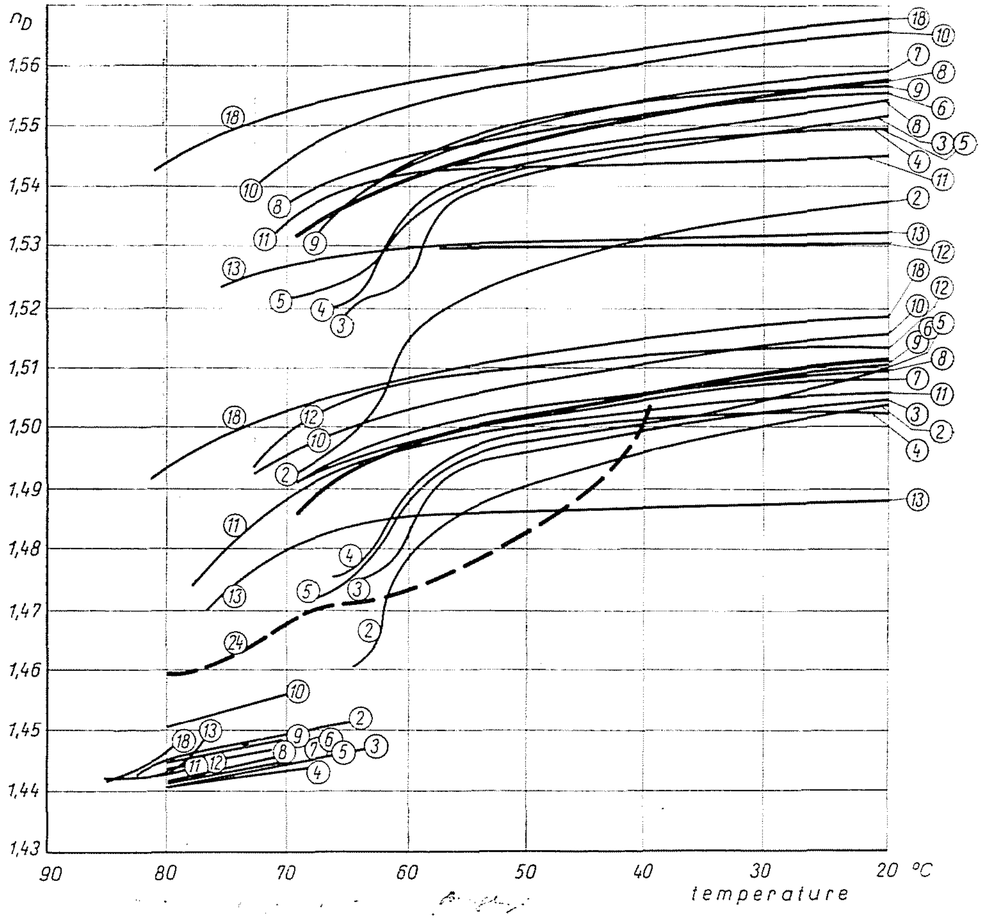

Fig. 6. Refraction vs. temperature curves of fractions separated by chromatography on silica gel from Sample 3

According to Table 4, the average molecular weights of fractions below 3—5 are less than 515. This limit would correspond to not more than 36 or 37 carbon atoms. Thus, on the basis of Fig. 1, it can be expected that these fractions contain some of the hexagonal modification, even if in a very narrow range of temperature. This expectation is jusitified by the shape of the relevant *n* vs. *t* curves. Experience shows that fractions 3—3 to 3—5, making up about 38 to 40 per cent by weight of the ceresin studied [11], have about 0.5 to 1.0 per cent of their available for their hexagonal modification.

As chromatographic separation progresses, or with increasing molecular weights, the *n* vs. *t* curves of fractions 3—6 to 3—10 will be drawn higher up both for liquid and solid samples. Here, as in the subsequent fractions, no hexagonal modification occurs any more.

This tendency of a shifting of refractive indices suffers a sudden change at fractions 3—11 to 3—13: in solid samples of these fractions refractive indices are lower again, double refraction rate, i.e. the difference between refractions pertinent to ordinary and extraordinary ray, becomes smaller, and the temperature gradient is practically zero. Considering that refractive indices of anisotropic substances, and the way temperature affects the refraction of these substances, and the optical double refraction of these substances are all functions of crystal structure, the findings just mentioned suggest that these fractions with a crystalline structure not yet identified assume a specific part in the crystallization peculiar to ceresins. These specific fractions constitute about 7 to 8 per cent by weight of the ceresin studied.

Unfortunately, fractions 3—14 to 3—17 were so small that no refractometric study of them was possible.

Chromatographic fraction 3—18 eluted with gasoline from the silica gel was the last one studied. The shape of its n vs. t curves conforms to the order shown, with the exception of fractions 3—11 to 3 –13, by the fractions progressively produced in the process of elution.

The fractions eluted with the chloroform-ethanol mixture deviate from all the fractions eluted with gasoline. They do not show double refraction, i.e. they have a single index of refraction in the solid phase. The n vs. t curves rise throughout the temperature range. In Fig. 6, these are represented by fractions 3—24.

Between 80° and 20 °C, the contraction of ceresin and of its fractions studied, is about 13 to 14 per cent, i.e. less than that of macrocrystalline paraffins. It is worthy of notice that in the fraction of lowest molecular weight eluted from ceresins, viz. in the fraction susceptible to allotropy, the contraction due to change of modification is about 3 per cent, about the same as that found for macrocrystalline paraffins.

For their valuable help accorded, the author wishes to express his thanks to Prof. L. Vajta, and Assoc. Prof. I. Szebényi, head of department.

Summary

There is an indirect way, via refractometry, to determine the contraction of paraffins. This is advantageous because the process of congelation, and of the change of modification, can be observed, and the contraction concomitant to these changes can be determined.

The congealing of macrocrystalline paraffins involves contraction amouting to about 9 per cent, change of modification causes 3 per cent of contraction. The shapes of refraction vs. temperature curves reflect a single change of modification between congealing point and 20 °C, both in macrocrystalline paraffins and their normal fractions obtained on molecular sieves.

The contraction of ceresin at congealing is about the same as that of macrocrystalline paraffins. Except for their low molecular weight fractions obtained in chromatography on silica gel, these substances do not suffer changes of modification. In low molecular weight ceresin fractions, the contraction due to change of modification is about the same as that in macrocrystalline paraffins.

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