

The Swelling of Polymethylenes in Low Molecular Weight Alkane Vapours

HELMER KOFOD*

Physical Chemistry Institute, University of Copenhagen, Denmark

This paper presents a part of a general research on thermodynamic properties of paraffin mixtures carried out by the late professor J. N. Brønsted and collaborators.

By means of an especially designed electromagnetic balance the swelling of a thin polymethylene film was measured when suspended in an atmosphere of a volatile alkane **. The equilibrium vapour pressure in the system was observed on a mercury manometer against absolute vacuum.

Polymethylenes of average molecular weights approximately 5 000, 20 000, 35 000 and 40 000 were examined. As a volatile alkane mainly *n*-hexane was used. The sample was of a very high degree of purity ($n_D^{25} = 1.37251$; $\rho^{25} = 0.65483$ g/ml; saturation vapour pressure $p^{22} = 13.25$ cm Hg). Preliminary experiments were carried out with *n*-heptane, *n*-octane, and 2,2,4-trimethylpentane. Vapour pressure isotherms were determined at 22° C, in a few cases also at 17° C and 27° C. The dependency of the swelling upon temperature, index (*i. e.* number of carbon atoms) of the two components and of the history of the individual film was investigated. The swelling was found to decrease with increasing temperature. The swelling of a given polymethylene film in low molecular alkanes at equal activity was found to decrease with increasing index. The effect of chain branching in the low molecular alkane seems to be to diminish the swelling relative to that of the normal compound.

The results in general proved consistent with current views on the structure of high polymer *n*-alkanes, a short survey of which is given. Owing to the peculiar mixed state of aggregation and the poorly defined molecular weights the data obtained for different polymethyl-

* Present address, Royal Danish School of Pharmacy, Copenhagen.

** The name "polymethylene" for the high polymeric homologues of the formula $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$ is preferred to the genetical "polyethylene" and the commercial "polythene".

enes were difficult to evaluate quantitatively. It is suggested that the observed differences in swelling are alone due to differences in the state of aggregation (degree of crystallinity) and that the swelling of amorphous polymethylene is in fact independent of its molecular weight.

It has been demonstrated that the expression $\frac{a}{c} = a e^{\beta c}$ holds for the mixtures investigated, a being the activity of the volatile alkane, c its concentration in the unit of moles per gram polymethylene, and a and β being constants.

In 1946 J. N. Brønsted and J. Koefoed¹ proposed the concept of congruence as the basis for a general prediction of the thermodynamic properties of alkane mixtures. The index ν of a mixture was defined as

$$\nu = x_1\nu_1 + x_2\nu_2 + \dots$$

where $x_1, x_2 \dots$ are the mole fractions of the components in the mixture and $\nu_1, \nu_2 \dots$ the indices, which for pure compounds are identical with the number of carbon atoms in the molecule. It was postulated that certain thermodynamic properties of congruent mixtures of n -alkanes, *i.e.* mixtures having the same index, are identical irrespective of the individuality of the components. In other words the thermodynamic properties of an alkane mixture is determined by its index.

The hypothesis was experimentally tested on three sets of binary mixtures of liquid n -alkanes, $C_6 + C_{16}$, $C_7 + C_{16}$ and $C_6 + C_{12}$ at 20° C. From vapour pressure measurements a simple relation was derived between the activity coefficient f_1 of a component 1 in the mixture, the index ν_1 of the component and the index ν of the mixture. The relation, $\log f_1 = B(\nu - \nu_1)^2$ was found to hold for mixtures of n -alkanes containing from 6 to 16 carbon atoms. The numerical value of B for this range was -0.00048 .

In order to test the hypothesis beyond these limits the scope has since been extended to straight chain alkanes of higher indices. Some of those in the range 16 to 36 have been investigated by other collaborators in this laboratory. The material has not yet been published. The present paper is devoted to binary mixtures of low molecular weight alkanes of index 6 to 8 and high polymeric alkanes of indices between 300 and 3 000.

Several difficulties are encountered when extending the scope from n -alkanes of short and medium chain length to long chain, high polymeric homologues. One is that the usual concepts of purity and identity grow more and more inapplicable. Up to about C_{80} it is still possible to obtain pure

chemical individuals characterized analytically and/or by way of unequivocal synthesis *e.g.* successive coupling of two identical alkyl groups. Pure alkanes of medium chain length can only be obtained synthetically from simple reaction mixtures containing few and widely different components, whereas an isolation of an individual alkane from a mixture of closely related homologues as *e.g.* natural products is extremely laborious if at all possible, even with the highly effective modern methods of separation.

In the group of polymethylenes with several hundreds or thousands of carbon atoms it is no longer possible to synthesize or isolate chemical individuals with a definite number of carbon atoms. The syntheses, mainly polymerizations, inevitably yield a mixture of alkanes with different chain lengths, although the process may be conducted so as to give products of a certain desired average molecular weight. A further "purification" may be accomplished by fractional precipitation and by other methods. A somewhat better characterization of a product is at hand, when not only the average molecular weight but also a distribution curve, giving the relative amounts of the various chain lengths, is known. It is evident that the index, defined as above, is a very useful term for precise characterization of high polymer *n*-alkanes, since it takes into account not only the average molecular weight but also the distribution curve. Unfortunately the experimental data necessary for the calculation of the index cannot be obtained with an accuracy comparable to that in the low molecular region.

Although polymerisations of simple compounds as ethylene with only two reaction centres should lead to "one-dimensional" unbranched carbon chains, there is nevertheless evidence² that a certain degree of branching cannot always be avoided. It is not certain, therefore, that the material used in our investigations is entirely of normal paraffin structure, and this must be born in mind when evaluating the results. It is, however, always a matter of *small* side chains, probably methyl groups, and their relative number decreases with increasing chain length (Ref.²⁴, p. 126).

In addition to the inaccessibility of individual well-defined long chain alkanes another difficulty also seriously interferes with the interpretation of some of the results, presented in this paper. That is the peculiar mixed state of aggregation of solid high polymers. A short summary will be offered below as a background for the discussion of results.

A. The structure of polymethylenes.

The molecular dimensions of polymethylene chains were established by C. W. Bunn in 1939 by means of X-ray methods³ and are reproduced in Fig. 1.

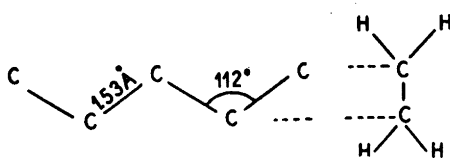


Fig. 1. Molecular dimensions of polymethylene chains (C. W. Bunn).

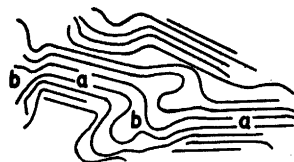


Fig. 2. Structure of solid polymethylene. a. crystalline parts. b. amorphous parts.

The dimensions are almost identical with those observed in alkanes of medium chain length *e.g.* $C_{20}H_{40}$ by A. Müller⁴ in 1928. The figure shows the carbon chain stretched, with all carbon atoms coplanar. Rotation is possible, outer conditions permitting, about any single bond in the chain resulting in a variety of "curled up" shapes *cf.* Fig. 2.

At room temperature polymethylenes are known to be semicrystalline solids *i.e.* they consist of randomly oriented microcrystalline parts, crystallites, Fig. 2 a, imbedded in amorphous parts, Fig. 2 b. The crystallites are crystalline in the sense that they are composed of straight chains regularly arranged parallel to one another, but they have no flat crystal faces. A single carbon chain may well penetrate several crystalline regions and also several amorphous regions in which the chain may be randomly curled up. This mixed order-disorder texture is common to many linear high polymers and was first suggested by K. H. Meyer and H. Mark⁵ in 1928 for natural fibres. In the case of polymethylene this view is strongly supported by X-ray crystallographic data, (Bunn and Alcock⁶), in that the crystallites have been shown to be considerably smaller than the average length of the carbon chains, and secondly the pattern display diffuse bands characteristic for amorphous solids and for liquids. The mechanical properties of polymethylene are easily explained on this basis. The substance is tough, often elastic, contrary to the typical crystalline alkanes containing up to about 80 carbon atoms. By stretching or "cold drawing" the chains in the amorphous regions are straightened and these as well as the crystallites are oriented parallel to the direction of stretching, thus increasing the overall orderliness of the material. This phenomenon has been proved by X-ray work⁷ and is observed directly as an increased tensile strength of the fiber.

The relative crystallinity obviously depends upon temperature. On heating the crystallinity decreases gradually. There is no well-defined transition point corresponding to the melting point of typically crystalline solids. By X-ray diffraction Bunn and Alcock⁶ observed a decrease of crystallinity, commencing at about 80° C. At about 100° C the value was *ca.* 50 %, at 120° it was zero,

and the substance appeared to be isotropic. The polymethylene sample used by these authors had an average m.w. of 17 000.

Hunter and Oakes⁸ in another polymethylene observed a crystallinity of 55 % at room temperature. A detectable decrease began at 70° C. At 100—120° the crystallinity was zero. The authors found indication that a state of equilibrium is quickly attained at temperatures above 60° C, whereas the order-disorder state is „frozen” below 60° C. These results were obtained by density measurements.

Similar observations were made by Raine, Richards and Ryder⁹ by investigation of the temperature dependency of the heat capacity. By this method changes in state could be observed from 50° C onwards. These authors found a relatively sharp transition point into nearly isotropic state at about 115° C. Even well above the “melting point” the molecules proved to be somewhat oriented, a fact suggested by Charlesby¹⁰ a few years earlier.

Richards¹¹ has investigated the effect of chain branching and molecular weight distribution on the “melting point”. Samples with the same average molecular weight, as indicated by intrinsic viscosities, were found to vary as much as 15° C in melting point, due to these reasons.

It is obvious from the above summary that the “melting point” of polymethylenes is of next to no value for the characterization of the products.

Polymethylenes are insoluble in low index alkanes at 20° C. On heating a homogeneous solution usually is formed at a certain temperature. For a mixture of polymethylene and *n*-heptane containing 5 % of the former the clarification temperature is 70—80° C, depending upon the molecular weight of the polymethylene. For *n*-hexane the corresponding temperature is above the boiling point^{19, p. 22}.

Whereas polymethylene does not dissolve in liquid low index alkanes at room temperature, these dissolve in solid polymethylene to a certain extent by swelling. This extreme form of the phase diagram and the fact that polymethylenes are completely non-volatile make the experimental approach particularly simple. The swelling in vapour phase is the subject for the following investigations.

EXPERIMENTAL

B. Apparatus.

The apparatus was designed by J. N. Brønsted and A. E. Lansner. It will be only briefly described here. It is shown diagrammatically in Fig. 3.

T is a water thermostat accurate to within $\pm 0.01^\circ$ C. E is the all glass equilibration chamber with the built-in electromagnetic balance. To the left arm of the beam is attached a permanent magnet shaped as a rod and dipping into the stationary coil C.

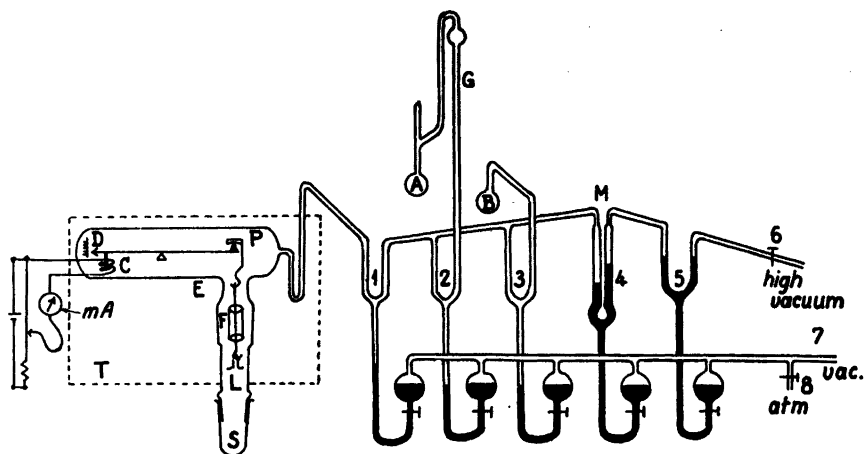


Fig. 3. Electromagnetic balance for weighing in an alkane atmosphere.

The latter is connected to the outer circuit by sealed-in platinum leads. The current through the balancing mechanism can be adjusted by means of the variable rheostat and read on the milliamperemeter mA with an accuracy ± 0.003 mA. All values were corrected according to a correction graph worked out by A. E. Lansner.

On the right hand knife of the beam a metal wire assembly is suspended, acting as a carrier for the film F and supplementary loads L. The plane P rested permanently on the knife but the lower parts of the carrier could be removed from and re-introduced into the chamber through the ground-glass-capped tube S emerging through the bottom of the thermostat.

To make a weighing the current was adjusted until an indicator mark on the left arm was brought to juxtaposition with the zero point of the indicator scale D. This adjustment was controlled visually through the glass wall of the thermostat and a special water-lens. With a total load of about 1.2 g, as in most experiments, the sensitivity of the balance was 0.03 mg, corresponding to 0.005 mA. When a standard procedure was followed, the readings were reproducible to within the sensitivity. As the absorbed weight of volatile alkanes usually have been between 1 and 15 mg, this means a relative accuracy of 3 to 0.2 %.

The zero current for the balance, even without film, was found to increase slightly with time, due to certain mechanical features of the beam. This phenomenon could, however, be completely eliminated by the following standard procedure. The current was adjusted to zero position of the balance. By means of a short-circuiting switch a "shock" of about 3 mA was applied to the coil, thus shaking the beam into a reproducible position. After 5 such "shocks" 5 independent re-adjustments were made and the reading taken each time. Again 5 shocks were applied and five readings taken. The arithmetic mean of these ten readings was used in the calculations. The relation between current i (mA) and load m (mg) was determined by means of excess loads of known weight. Results are given in Fig. 4. They were determined at 22° C and *in vacuo*. The relation is linear and $\Delta m = 6,1 \Delta i$. This value was used throughout this paper. It did

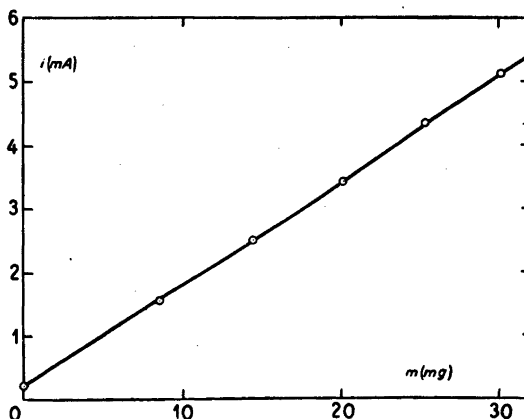


Fig. 4. Relation between current i and load m .

not alter perceptibly with temperature within the limits concerned. Buoyancy effects were found to be negligible under the given conditions.

The right hand parts of the apparatus in Fig. 3 serve the purpose of establishing and measuring the vapour pressure of the volatile alkane in the equilibration chamber. Communication between the various parts of the all-sealed system is controlled by the mercury valves 1–5 operated by means of a vacuum pump and the respective stopcocks. A and B are reservoirs for the volatile alkane. A, which also contains the drying agent (phosphorus pentoxide) is connected to the rest of the system by the tube G, which is of sufficient height to permit trapping of all the air-free alkane in A, when the atmosphere is admitted to the apparatus during exchange of films *etc.*

The equilibrium vapour pressure is read directly on the mercury manometer M against a high vacuum, *i.e.* effectively against the vapour pressure of mercury at 20° C, which amounts to 0.001 mm Hg. The difference in height of the two mercury menisci was read in the ordinary way using a cathetometer provided with a vernier. The accuracy was ± 0.005 cm. Obviously the temperature of the manometer, *i.e.* room temperature had to be kept approximately constant during measurements, and the manometer was protected from heat radiations. During evacuation of the equilibrium chamber and accessories, direct connection to the high vacuum pump was procured by emptying the manometer tubes by means of valve 4.

The effective volume during equilibration and measurements was, apart from the ground-glass-cap S, limited by either sealed glass or mercury surfaces, the involved parts of the glass tube system having been blown in one piece without stopcocks.

C. Materials.

n-Hexane. At the time, when the experimental work was carried out, no hexane of sufficient purity was commercially available. Fractionation of a technical grade product in a 60-plate column yielded a small quantity of about 99 % pure hexane, $n_D^{25} = 1.37300$, $\rho^{25} = 0.65574$. The impurity was an isomer. This sample was used for the small series no. 5 given in Table 2. In all other series a product of very high purity was used. It was made synthetically from pure propanol-1, which was converted into 1-bromopropane.

The *n*-hexane was finally obtained in 70 % yield by a Wurtz synthesis. Only constant boiling fractions of the intermediates were used and the final product was subjected to careful fractionation according to A. Klit¹³ in a 60-plate column. It had an absolutely constant boiling point of 68.9° C at 760 mm (Timmermans and Martin¹⁴ give 68.80°). The refractive index was also constant $n_D^{25} = 1.37251$ over the whole fraction. The most reliable value extracted from the literature¹⁵ seems to be 1.3751 at 20° C; using $dn/dt = -0.00056$ we get $n_D^{25} = 1.3723$. The density was found to $\rho^{25} = 0.65483$ g/ml. Remeasurements on the hexane sample used for the investigations by Brønsted and Koefoed¹ showed complete identity.

n-Heptane. The preparation described in a previous paper¹ was used.

n-Octane was obtained by fractional distillation of a synthetical product. It had a constant boiling point 124.7° C at 760 mm.

2,2,4-trimethylpentane, "iso-octane". A commercial product holding 99 % purity was distilled. The intermediate fraction used had a boiling point 99.3° C at 760 mm. Ref.¹⁶: 99.3° C at 760 mm.

The last two alkanes of a less high purity were used only for some preliminary experiments.

The values of the saturation vapour pressures, used in the calculations, were determined experimentally in this laboratory and are given in Table 1. After the experimental part of this work was terminated, The National Bureau of Standards has published "Selected Values of Properties of Hydrocarbons" under "The American Petroleum Project". In the last column (N.B.S.) are given the values calculated from the Antoine equation $\log_{10} p = A - \frac{B}{C + t}$ using the values of *A*, *B* and *C* from the 1948-sheets of the said publication. They agree satisfactorily with our data.

Table 1. Saturation vapour pressures of the volatile components.

	<i>t</i>	<i>p</i>	<i>p</i> (N.B.S.)
<i>n</i> -Hexane	17° C	10.57	10.57 cm Hg.
	22° C	13.25	13.26
	27° C	16.47	16.48
<i>n</i> -Heptane	22° C	3.93	3.93
<i>n</i> -Octane	22° C	1.18	1.176
2,2,4-Trimethylpentane	22° C	4.29	4.268

Xylene was obtained by distillation of a commercial preparation. The fraction used had a boiling range of 137–144° C and consisted of a mixture of isomers of unknown but constant composition. It was only used as a solvent during preparations of polymethylene films. The content of non-volatile impurities (100° C) was less than 0.03 pro mille.

Polymethylenes. All the samples were supplied by H. Mark's laboratories, Polytechnic Institute of Brooklyn. The average molecular weights indicated by the supplier were 5 000, 20 000, 35 000 and 40 000. In the following the polymethylenes will be characterized by their indices, *i.e.* number of carbon atoms, 360, 1 430, 2 500 and 2 860 respectively. These values are calculated

from the above molecular weights by dividing by 14 (CH_2), and it should be clearly understood that they are approximate values.

All four polymethylenes were tested for presence of low molecular weight material. The substance was dissolved in xylene at 90°C and precipitated on standing at 20° . By evaporation at 100° of the mother liquor from repeated experiments it was shown, that all the polymethylenes were insoluble in xylene at 20°C and secondly, that they did not contain impurities soluble in xylene at 20°C , such as low molecular weight alkanes.

It was found that the polymethylenes did not loose in weight on heating to 130°C for 50 hours *in vacuo*. Consequently they did not contain volatile material, nor did any decomposition take place under the conditions at which the films were prepared (*vide infra*).

For the purpose of roughly checking the stated average molecular weights relatively to one another some viscosimetric measurements were undertaken. The time of efflux of solutions in xylene containing 0.5 g in 100 ml was determined in an Ostwald viscometer at 85°C . At this temperature all the polymethylenes formed homogeneous solutions. At 75°C , which was first tried, C_{1430} and C_{2500} dissolved clearly in the above concentration, whereas C_{360} and C_{2860} (!) did not.

In Table 2 τ is the time of efflux in sec. It was reproducible to within at least ± 2 sec. η is the viscosity in centipoise. Let ρ be the density at 85°C , then it is well known that $\eta = C\rho\tau$, where C is a constant characteristic of the apparatus. By calibration of the viscometer against water the value $C = 5.26 \cdot 10^{-5}$ was found at 85°C . According to Staudinger²²

$$\frac{\eta_{\text{sp}}}{c} = \frac{\eta - \eta_0}{\eta_0 \cdot c}$$

where η_{sp} is the specific viscosity, subscript 0 refers to the solvent and c is the concentration of solute. For the present purpose we are justified in regarding the densities of the solutions equal to that of the solvent, hence

$$\frac{\eta_{\text{sp}}}{c} = \frac{\tau - \tau_0}{\tau_0 \cdot c}$$

The relation between the index and viscosity is according to W. Kuhn²³

$$\lim_{c \rightarrow 0} \frac{\eta_{\text{sp}}}{c} = k \cdot \nu^\alpha$$

k and α are constants depending on the nature of the solute. For $\alpha = 1$ the expression is identical with the original Staudinger equation, for flexible molecules as polymethylene we have $\alpha < 1$ ^{22, p. 223}. For a rough comparison

we choose the concentration 0.5 %, without extrapolating to zero. Provided α is constant for the series of polymethylenes investigated the relation of $\log \frac{\eta_{sp}}{c}$ to $\log \nu$ should be linear.

Table 2. Viscosity of 0.5 % polymethylene in xylene at 85° C.

ν	τ (sec.)	η	η_{sp}/c	$\log \nu$	$\log [\eta_{sp}/c]$
360	87	0.370	20	2.56	1.30
1430	128	0.545	124	3.16	2.09
2500	130	0.552	129	3.40	2.11
2860	151	0.642	182	3.46	2.26
xylene	$\tau_0 = 79$	0.336			

A plot of the values in the last two columns of the table shows this to be roughly true, at least the viscosity increases in the same order as the indices.

D. Experimental procedure.

The polymethylene films were generally prepared in the following way. A suitable quantity of polymethylene, usually 0.2 g was dissolved in *ca.* 5 ml pure xylene by heating to 90° C. The hot solution was poured into a rectangular brass pan 5 × 6 cm, carefully levelled. The solvent was slowly evaporated at 100° C, the last traces being removed in a vacuum drying oven. After removal from the mould and trimming, the dimensions of the film were approximately 4 × 5 × 0.005 cm. Thicker films were unsuitable owing to slow equilibration. A list of all the employed films and their data is given in Table 3.

Suitable quantities of the volatile alkane and drying agent (phosphorus pentoxide) were introduced in bulb A (Fig. 3). The bulb was cooled to -80° C in a mixture of solid carbon dioxide and acetone and then sealed off. The equilibration chamber was closed, the cap S being lubricated with high vacuum grease. All valves were opened and the entire system including the contents of bulb A, still being kept at -80° C, was evacuated with the high vacuum pump. In order to secure removal of all traces of air from the alkane sample, this was distilled several times between bulbs A and B and evacuated at -80° C after each distillation. During the distillations valves 1 and 4 were closed. The de-aeration was continued until the vapour pressure of the alkane

Table 3. Data of the polymethylene films.

Film no.	$\overline{M.W.}$	ν	Net weight in air (grams)	Surface (cm ²)	Average thickness (cm)	History of preparation
1	20 000	1 430	0.0955	38	0.005	Cylindrical film prepared by evaporation from a xylene solution at 100° C in a horizontal, rotating testtube. Dried <i>in vacuo</i> at 100° C to constant weight.
2	20 000	1 430	0.1020	4.5	0.05	A hot solution in xylene was cooled, the precipitated, swollen polymethylene was dried <i>in vacuo</i> at 20° C to constant weight.
3	20 000	1 430	0.1569	36	0.01	Plane film prepared by evaporation from a xylene solution at 100° C. Dried <i>in vacuo</i> at 100° C to constant weight.
5	20 000	1 430	0.1650	54	0.005	As film no. 3
6	35 000	2 500	0.1234	50	0.005	As film no. 3
7	35 000	2 500	0.1153	46	0.005	As film no. 3
8	5 000	360	0.1487	incoherent flakes		As film no. 3
10	40 000	2 860	0.1166	46	0.005	As film no. 3
10a	40 000	2 860	0.1151			Film no. 10 was soaked in liquid xylene at 50° C over night, dried <i>in vacuo</i> at 20° C.
10b	40 000	2 860	0.1150			Film no. 10a was soaked in liquid xylene at 50° C for 48 h, dried <i>in vacuo</i> at 80° C.
10c	40 000	2 860	0.1150			Film no. 10b was soaked in liquid xylene at 50° for 2 h, dried at 20° C <i>in vacuo</i> .
10d	40 000	2 860	0.1150			Film no. 10c was heated <i>in vacuo</i> to 100° C for 3 h.

sample at -80°C was less than the accuracy of measurements, 0.005 cm. For hexane, being the most volatile of the alkanes measured, the vapour pressure at this temperature should be 0.005 cm, for the other alkanes much less.

The dry and de-aerated alkane was stored in bulb A, while the atmosphere was again admitted to the high vacuum side. The film was cylindrically wound up on the carrier, the weight of which was 0.8202 g. The accurate weight of the film in air (approximately 0.1 g) was determined as a difference. By hanging on supplementary weights the total weight of the film + carrier was increased to approximately 1.17 g, which corresponded to a convenient zero current of 0.187 mA. The assembly was then suspended on the electromagnetic balance, the equilibration chamber closed and the "air reading" on the milliamperemeter taken. Then the system was evacuated for several hours, until the reading on the meter did not alter on further evacuation. This reading will be termed the "zero current". If the film had lost in weight, *i.e.* zero current lower than air reading, then the absolute net weight of the film was corrected accordingly before entering into the calculations. The corrections were very small, usually 0.1 to 0.2 mg (adsorbed air and moisture).

After the determination of the zero current and the corrected net weight of the film the pump was cut off by operating valve 5 and stopcock 6. Mercury was admitted into the manometer M, and by operating valve 2 and suitable heating and cooling of the bulb A, a sufficient quantity of volatile alkane was admitted to the evacuated system. In this way it was possible to establish approximately any desired vapour pressure, ranging from zero to the saturation vapour pressure of the alkane in question at the lowest temperature in the system, *i.e.* room temperature (manometer) or thermostat temperature, whichever was the lowest.

In the following the results of fifteen series of measurements will be discussed. All the relevant data are collected in Table 4. The number of the film in column 6 refer to Table 3. Column 7 contains the equilibrium vapour pressure p_{ν} of the volatile component in cm Hg. Column 8 contains the saturation fraction or vapour activity a_{ν} . The values of saturated vapour pressures $p_{\nu_1(\nu_1)}$, applied in the calculations, are given in Table 1. In column 9 g_{ν} denotes weight in grams of component ν in the mixture. Thus the column gives gram absorbed volatile alkane by 1 gram polymethylene. The tenth column contains the concentration c of the volatile component in millimoles per gram polymethylene. The values in the last column are calculated from those in column 8 and 10.

Table 4.

1	2	3	4	5	6	7	8	9	10	11
Series	t (°C)	Volatile component	v_1	Poly- methy- lene v_2	Film no.	p_{v_1}	$\frac{p_{v_1}}{P_{v_1}(v_1)} = a_{v_1}$	$\frac{g_{v_1}}{g_{v_2}}$	$\frac{g_{v_1} \cdot 10^3}{g_{v_2} \cdot M_{v_2}} = c_{v_1}$	$\log \frac{a_{v_1}}{c_{v_1}}$
2	17	<i>n</i> -hexane	6	1 430	1	2.100	0.1987	0.0137	0.159	0.097
						5.535	.5237	.0460	0.534	-0.009
						8.650	.8184	.0936	1.087	-0.123
						9.620	.9101	.1183	1.374	-0.179
						9.88	.9347	.1274	1.480	-0.199
						10.09	.9546	.1349	1.567	-0.215
						10.095	.9550	.1381	1.604	-0.225
						10.285	.9730	.1512	1.756	-0.256
						4.800	.4541	.0401	0.466	-0.011
						7.325	.6930	.0733	0.851	-0.089
						3	17	<i>n</i> -hexane	6	1 430
9.640		.1733								
4.885		.0431								
5.805		.0548								
7.170		.0782								
9.040		.1382								
1.150		.0991								
0		.0028								
1.850		.0141								
8.550		.1191								
8.160		.1057								
4	22	<i>n</i> -hexane	6	2 860	10	8.845	.6676	.0521	0.605	0.043
						9.985	.7536	.0625	0.725	0.017
						8.045	.6072	.0455	0.528	0.061
						3.625	.2736	.0191	0.222	0.091
						6.570		.0368		
					10a	11.820		.1001		
						9.220		.0640		
						10.980		.0860		
						8.060		.0516		
						6.140		.0356		
					10b	9.315	.7030	.0536	0.622	0.053
						11.990	.9049	.0851	0.988	-0.038
						5.240	.3955	.0258	0.299	0.122
					10c	7.455		.0436		
						12.020		.1063		
	9.815		.0694							
	11.070		.0876							

Table 4 continued.

					10d	11.580	.8740	.0762	0.885	-0.006
						8.595	.6487	.0476	0.553	0.069
						5.530	.4174	.0268	0.311	0.128
						2.185	.1649	.0100	0.116	0.152
						4.435	.3347	.0206	0.239	0.146
						3.615	.2728	.0161	0.187	0.164
						0.915	.0691	.0046	0.053	0.155
5	22	<i>n</i> -hexane	6	1 430	1	0.925	0.0698	0.0053	0.062	0.052
						2.037	.1537	.0122	0.142	0.034
						4.430	.3343	.0269	0.312	0.030
						9.040	.6823	.0740	0.859	-0.100
6	22	<i>n</i> -hexane	6	1 430	1	1.605	.1211	.0089	0.103	0.070
						3.695	.2789	.0217	0.252	0.044
						7.220	.5449	.0507	0.589	-0.034
						7.24	.5464	.0497	0.577	-0.024
						9.01	.6800	.0708	0.822	-0.082
						9.40	.7094	.0761	0.884	-0.095
						9.99	.7540	.0846	0.983	-0.115
						11.07	.8355	.1064	1.236	-0.170
						11.06	.8347	.1067	1.239	-0.171
						11.53	.8702	.1185	1.376	-0.199
						11.53	.8702	.1188	1.380	-0.221
						10.53	.7947	.0991	1.151	-0.161
						10.51	.7932	.0976	1.133	-0.155
						8.08	.6098	.0640	0.743	-0.086
						5.96	.4498	.0408	0.474	-0.023
						4.69	.3540	.0307	0.357	-0.004
						4.72	.3562	.0304	0.353	0.004
7	17	<i>n</i> -hexane	6	1 430	5	4.695	.4442	.0330		
						9.540	.9026	.1006		
						7.340	.6944	.0623		
						8.795	.8321	.0846		
						10.165	.9617	.1169		
						10.330	.9773	.1241		
8	22	<i>n</i> -hexane	6	1 430	5	11.190	.8445	.0924		
						11.925	.9000	.1042		
						7.975	.6019	.0534		
						9.655	.7287	.0704		
						5.765	.4351	.0348		
						2.875	.2170	.0155		
						12.235	.9234	.1090		

Table 4 continued.

9	27	<i>n</i> -hexane	6	1 430	1	4.590	.2787	.0216	0.251	0.045
						7.090	.4305	.0375	0.436	-0.006
						8.800	.5343	.0508	0.590	-0.043
						10.455	.6348	.0657	0.763	-0.080
						11.790	.7158	.0798	0.927	-0.112
						9.425	.5723	.0567	0.659	-0.061
						6.345	.3853	.0341	0.396	-0.012
10	17	<i>n</i> -hexane	6	1 430	3	1.885		.0106		
						9.000		.0856		
11	22	<i>n</i> -hexane	6	360	8	9.890	.7464	.0321	0.373	0.301
						7.995	.6034	.0220	0.255	0.374
						7.145	.5393	.0189	0.219	0.391
						3.340	.2521	.0053	0.062	0.609
						5.420	.4091	.0120	0.139	0.469
						11.495	.8676	.0425	0.493	0.246
						11.380	.8589	.0443	0.514	0.218
12	22	<i>n</i> -hexane	6	2 500	6	4.175	0.3151	0.0237	0.275	0.058
						7.045	.5317	.0478	0.555	-0.019
						9.825	.7415	.0864	1.003	-0.131
						11.790	.8898	.1323	1.535	-0.237
						11.180	.8438	.1195	1.387	-0.216
						6.545	.4940	.0455	0.528	-0.029
						8.650	.6528	.0695	0.807	-0.092
						10.725	.8094	.1054	1.223	-0.179
13	22	<i>n</i> -hexane	6	2 500	7	4.700	.3547	.0258	0.300	0.073
						10.580	.7985	.0885	1.027	-0.019
						11.845	.8940	.1159	1.345	-0.177
						8.525	.6434	.0615	0.714	-0.045
14	22	<i>n</i> -heptane	7	2 860	10d	2.520	.641	.0476	0.475	0.130
						3.265	.831	.0699	0.698	0.076
						2.295	.584	.0424	0.423	0.140
						0.500	.127	.0090	0.090	0.149
						1.565	.398	.0260	0.259	0.186
15	22	<i>n</i> -octane	8	2 860	10d	0.715	.606	.0450	0.394	0.187
						0.975	.826	.0697	0.610	0.131
						0.230	.195	.0125	0.109	0.253
						1.140	.966	.1000	0.876	0.042
						0.230	.195	.0127	0.111	0.245
						0.790	.670	.0517	0.453	0.170

Table 4 continued.

						0.850	.720	.0569	0.498	0.160
						0.595	.504	.0360	0.315	0.204
						1.030	.873	.0781	0.684	0.106
16	22	"iso-octane"	8	2 860	10d	3.180	.7421	.0505	0.442	0.225
						0.845	.1972	.0101	0.088	0.351
						2.025	.4726	.0277	0.243	0.289
						3.880	.9055	.0718	0.629	0.158
						4.180	.9755	.1077	0.882	0.044

E. Equilibration time.

The time elapsed from the establishment of a certain vapour pressure until an equilibrium is set up between the gaseous phase and the binary mixture represented by the swollen polymethylene film obviously depends on the dimensions of the film. Films about 0.005 cm thick were found suitable for measurements. Typical equilibration curves are shown in Fig. 5.

The quantity of hexane in milligrams absorbed by a polymethylene film (C_{1430}) is plotted against a time basis. The applied vapour pressure is for curve 1 0.925 cm Hg, the temperature 22° C. Equilibrium is attained after

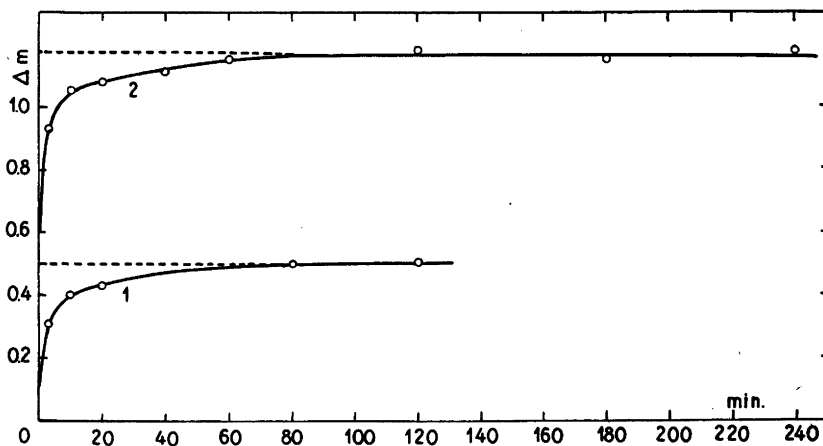


Fig. 5. Equilibration time. Film no. 1 (C_{1430}), swelling in n-hexane at 22°. Absorbed n-hexane in milligrams against minutes after alteration of vapour pressure.

- 1: Vapour pressure altered from 0 to 0.925 cm Hg.
- 2: Vapour pressure altered from 0.925 to 2.037 cm Hg.

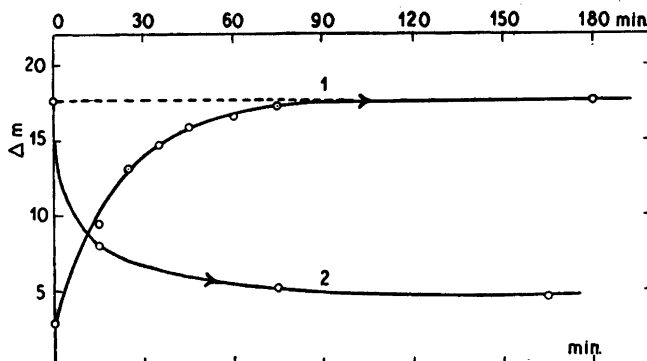


Fig. 6. Equilibration time. Film no. 2 (C_{1430}), thick film, swelling in *n*-hexane at 17° . Absorbed *n*-hexane in milligrams against minutes after alteration of vapour pressure.

- 1: Vapour pressure altered from 3.85 to 9.64 cm Hg.
- 2: Vapour pressure altered from 9.64 to 4.89 cm Hg.

1½ hour. Curve 2 represents the next step in the same series of measurements (Table 4, series no. 5). The vapour pressure has been altered to 2.037 cm by admitting more hexane into the system. Here, and in fact in all our measurements on thin films, the equilibration time was less than 2 h and practically independent of the sign and magnitude of the preceding pressure change.

Obviously complete equilibrium was secured in any single measurement by following the readings on the milliamperemeter and the manometer usually 20 min. after two subsequent readings having been identical.

Fig. 6 shows equilibration curves for a thicker film (no. 2; 0.05 cm) and somewhat higher hexane pressures. The curves are more flat, and safe equilibrium was only attained after 3–4 hours or more with films more than 0.005 cm thick.

F. Absorption or adsorption. Dependency of absorption upon the dimensions of the film.

Although it is not *a priori* very likely that the weight increase of a polymethylene film in an alkane atmosphere is due to adsorption on the surface, this possibility was tested by comparison of film no. 1 and 2 (Table 3), from the same batch of material, of approximately equal weight but differing in shape. No. 1 had a total surface of *ca.* 40 cm², no. 2 of only 4 cm². If due to adsorption only, the weight increase of film no. 2 should be smaller than that of no. 1. Experimental results plotted in Fig. 7 show to the contrary. Here

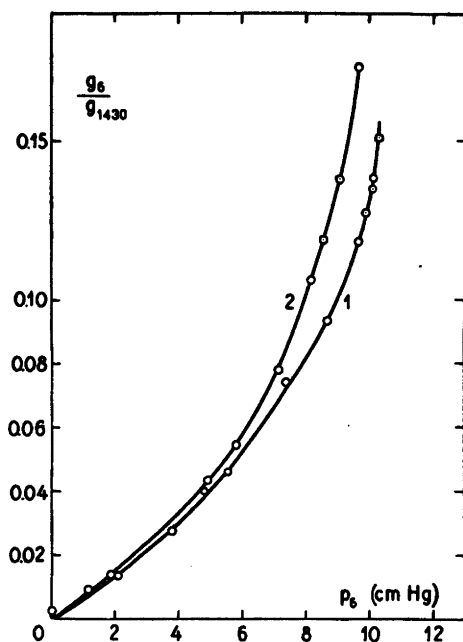


Fig. 7. Hexane absorption by polymethylene C_{1430} at 17° , dependency on the dimensions of the film. Grams absorbed hexane per gram polymethylene against equilibrium vapour pressure.

- 1: Film no 1, series 2 (thin film, large surface).
 2: Film no 2, series 3 (thick film, small surface).

and in the following g signifies weight in grams, thus g_6/g_{1430} , the ordinate, is grams n -hexane absorbed per gram polymethylene of average index 1430. The abscissa p_6 is the equilibrium vapour pressure of the volatile component, *in casu* n -hexane, in cm Hg. It is evident, that for all pressures film no. 2, having the smaller surface, shows the larger weight increase per gram. The reason why the two curves do not coincide, as could be anticipated on grounds of absorption, is to be sought in the history of preparation of the two films, *vide* section H.

There are no other indications that adsorption phenomena seriously interfere with the results in this paper, except perhaps in those parts of the swelling curves that correspond to vapour pressures very close to the saturation pressure; in Fig. 7 this is $p_{6(s)} = 10.57$ cm. These extreme parts of the curves should therefore be treated with some reserve.

G. Reproducibility of absorption in an individual film at low temperatures. Hysteresis?

The equilibrium composition of an individual swollen film in the atmosphere of a given alkane only depends upon the temperature and the applied vapour pressure, but seems to be independent of the preceding pressure changes

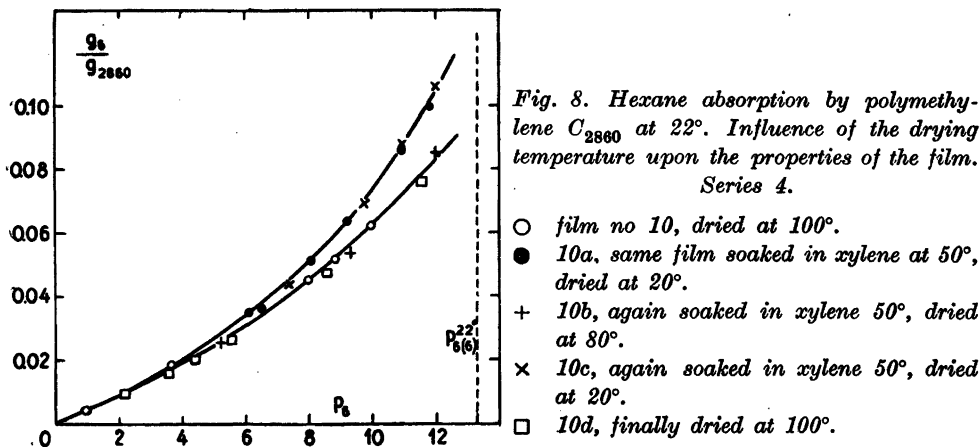
in the series of measurements. Thus an absorption value could be reproduced without systematic deviations, when the corresponding vapour pressure was re-established later in the series. This means that the original structure, *e.g.* the degree of crystallinity, of the film is unaltered by the swelling, at least when using hexane vapours and not exceeding 27° C. To be sure, in any series of measurements, a number of readings were taken at increasing values of vapour pressure p , followed by a number of readings at decreasing values, or readings were taken going up and down the pressure scale several times. Fig. 10 (series 6, Table 4) gives an idea of the maximum error, the arrows indicating whether a point is a member of an ascending or a descending series. Series 6 was the very first measured, it is actually composed of three series of observations made by two different persons during a period of 10 days. It does therefore correspond to exceptionally unfavourable conditions. In all other series the reproducibility is much better, *vide e.g.* the points for film no. 5 in the same figure (squares). The sequence is as indicated in Table 4, series 8 from top to bottom.

Frequently the net weight of the film was re-determined at the end of a series after complete pumping out of the volatile component. The original value was always found.

H. Structural changes in the film at higher temperatures.

Some experiments were carried out in order to estimate, how far the properties of a polymethylene film could be altered by swelling at higher temperatures and drying again at different temperatures. The results are given in Fig. 8. The same film, no. 10, was measured, then soaked in liquid xylene at 50° C (polymethylene is insoluble at this temperature), carefully freed from xylene by drying *in vacuo* at 20° C (no. 10 a), again soaked and dried at 80° C (no. 10 b), again soaked and dried at 20° C (no. 10 c) and finally without further soaking dried at 100° C (no. 10 d). These treatments did not appreciably lower the net weight of the film (*cf.* Table 3 column 4). A series of measurements of the hexane absorption was taken after each treatment. In Fig. 8 grams absorbed hexane per gram polymethylene is plotted against the equilibrium vapour pressure in cm Hg.

It is evident that the points group themselves about two curves, one of which represents "cold dried" films and the other "warm dried" films. It thus appears that two fairly reproducible states of aggregation of polymethylene are set up, corresponding to a lower and a higher temperature. None of these states could probably be thought of as representing a thermodynamic equi-



librium between crystalline and amorphous structure, particularly not the "low temperature state", which is without doubt a more or less frozen metastable state.

The "high temperature state" shows the smaller absorption. This fact could be accounted for by assuming a larger degree of crystallinity in that state, which assumption is not *a priori* unlikely, as at the moderately high temperatures $80-100^\circ\text{C}$, well below the transition region, crystallization should occur more rapidly than at room temperature. Later work¹⁷ has provided evidence of a gradual but very slow increase in crystallinity even at room temperature. It is not surprising either that the state of lower crystallinity can be restored by soaking the "warm dried" film in liquid xylene at 50°C , because the swelling, although taking place in the amorphous regions, might, to a certain degree, affect the interfaces of the crystallites forcing the parallel chains somewhat apart, and consequently reducing the overall relative crystallinity. This effect is not perceptible in our absorption measurements carried out at lower temperatures, $< 27^\circ\text{C}$.

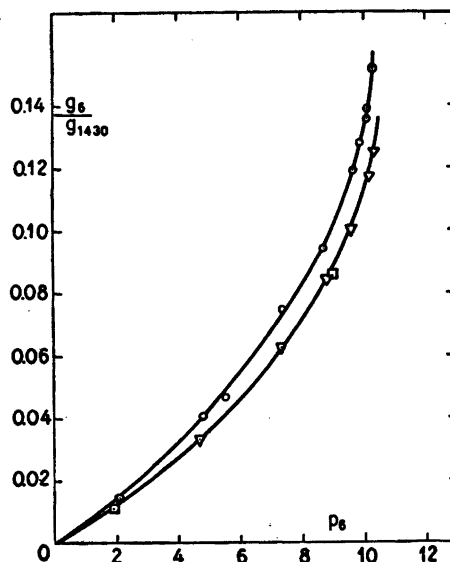
The two curves in Fig. 8 probably give an idea of the maximum deviations to be expected, when two films are prepared from the same material and no special care is taken to standardize the operations.

Films no. 1 and 2 (Fig. 7) constitute such a pair of films, no. 1 having been dried at 100°C , no. 2 at 20° . It is interesting to notice, that here again the "cold dried" film shows the larger absorption.

Not only the drying temperature but also the rate of the drying and other conditions influence the properties of the film. Thus in Fig. 9 film no. 1 (circles) shows a larger absorption than films no. 3 and 5, although they were

Fig. 9. Hexane absorption by polymethylene C_{1430} at 17° . Comparison of different films of the same material.

- film no 1, series 2.
- 3, series 10.
- ▽ 5, series 7.

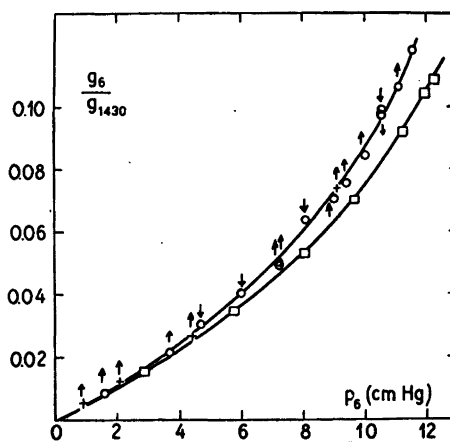


made from the same material and dried at the same temperature, 100°C . No. 1, however, was prepared by evaporation of the solvent in a horizontal rotating testtube (cf. Table 3, last column) whereas no. 3 and 5 were plane films, left undisturbed during evaporation. As we should expect, the "undisturbed" crystallization leads to a higher degree of crystallinity, as indicated by the lower absorption of films no. 3 and 5. Fig. 10 giving results obtained with films no. 1 and 5, but at another temperature, shows similar features.

On the other hand, when a standard procedure of preparation is strictly adhered to, it seems possible to obtain two films of equal properties. Thus in

Fig. 10. Hexane absorption by polymethylene C_{1430} at 22° . Comparison of two films of same material.

- film no 1, series 6
- 5, series 8
- + 1, series 5
- ↑ observation in a series of increasing vapour pressures.
- ↓ observation in a series of decreasing vapour pressures.



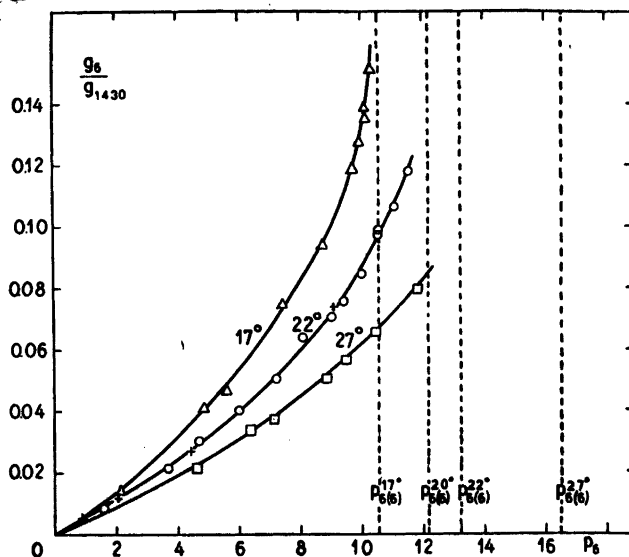


Fig. 11. Hexane absorption by polymethylene C_{1430} at different temperatures. Film no 1. Grams absorbed *pr.* gram polymethylene against equilibrium vapour pressure.

- Δ 17°, series 2
- \circ 22°, series 6
- + 22°, series 5
- \square 27°, series 9

Saturation pressures indicated by the dotted lines.

Fig. 9 the data of film no. 3 (squares) and film no. 5 (triangles) fit the same curve. The material however is scarce, and the consistency may be incidental rather than significant, so much the more as another pair of films, no. 6 and 7, prepared from C_{2500} under identical conditions shows quite considerable deviations, *vide* Fig. 15, triangles.

I. Hexane absorption by polymethylene C_{1430} at different temperatures.

Fig. 11 illustrates the temperature dependency of the swelling of polymethylene in hexane vapours. Film no. 1 was used for all measurements. Grams hexane absorbed by one gram polymethylene is plotted against the equilibrium vapour pressure p_6 . The swelling at any given vapour pressure decreases with increasing temperature. As the applied vapour pressure approaches the saturation pressures $p_{6(6)}$ at the relevant temperature, indicated

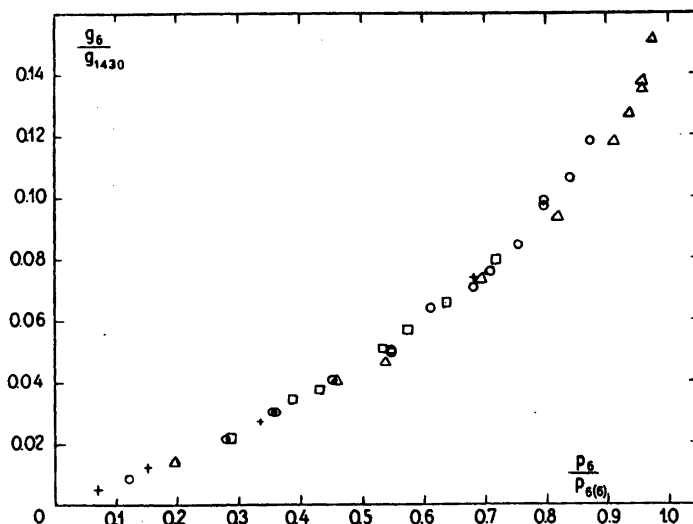


Fig. 12. Hexane absorption by polymethylene C_{1430} at different temperatures. Film no 1. Grams absorbed per gram polymethylene against saturation fraction.

- Δ 17°, series 2
- \circ 22°, series 6
- + 22°, series 5
- \square 27°, series 9

by the vertical dotted lines, measurements become impossible because of condensation on the film and on the balance. For the two series measured at 22° and 27° C the saturation pressure at room temperature (20° C) is the limiting value, at which condensation takes place in the manometer system. The values of saturation pressures are those given in Table 1. For $p_6 = p_{6(20)}$ the absorption probably reaches a finite value, *i.e.* that valid for swelling in liquid hexane. Then a new phase is formed, consisting of pure liquid hexane, since polymethylene C_{1430} is insoluble in hexane in the temperature range covered by the experiments. Similar behaviour is well known for other binary mixtures of a high polymer and a low molecular compound¹⁸.

When the absorption is plotted against the saturation fraction (vapour activity) $p_6/p_{6(20)}$ as shown in Fig. 12 the three curves valid for 17°, 22° and 27° C respectively, very nearly coincide, showing very little effect of temperature changes. The tendency is toward a small increase of absorption with increase of temperature, which is also demonstrated in Fig. 14 (see below) but this point needs further confirmation by measurements at higher temper-

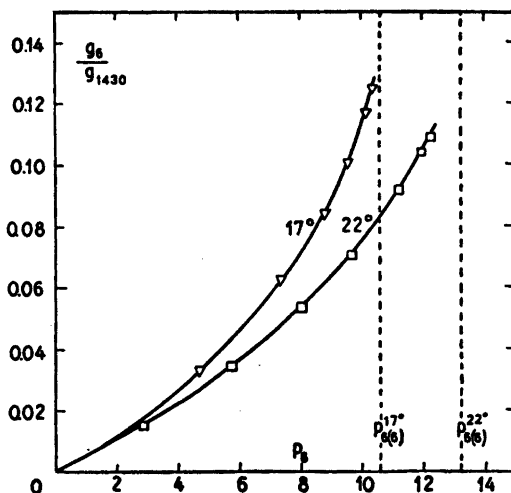


Fig. 13. Hexane absorption by polymethylene C_{1430} at different temperatures. Film no. 5.

- ∇ 17°, series 7
 \square 22°, series 8

atures. A positive temperature coefficient has been found for the swelling of other high polymers, see for instance¹⁸.

A rough estimate of the solubility of liquid *n*-hexane in polymethylene C_{1430} can be obtained by extrapolating the graph in Fig. 12 to $p_6/p_{6(6)} = 1$. The value probably is between 0.15 and 0.20 gram per gram polymethylene at room temperatures.

Fig. 13 and 14 illustrates the data obtained with another film (no. 5) of the same material at 17 and 22° C. The results are concordant with the previous ones, but the absolute values of absorption differ, because the two films have a different degree of crystallinity.

J. The absorption of *n*-hexane by polymethylenes of different indices.

Fig. 15 shows the vapour pressure isotherms at 22° C for films prepared similarly from polymethylenes with the indices indicated at the end of the curves. The volatile alkane is *n*-hexane.

The results do not on the whole permit definite conclusions. For comparison the isotherm for crystalline $C_{36}H_{74}$ is also given. This substance does not absorb hexane under similar conditions and the isotherm coincides with the

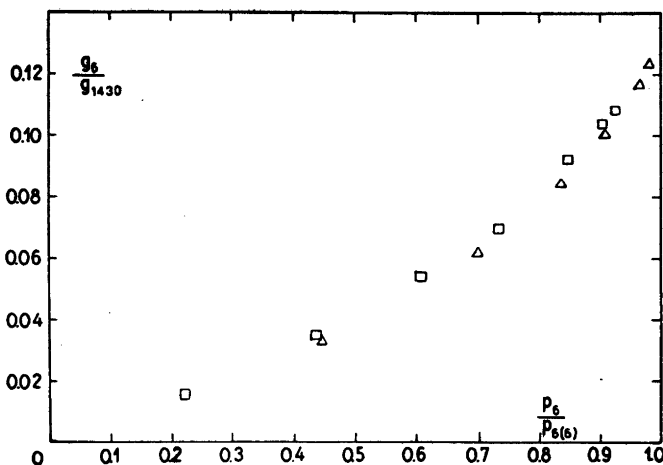


Fig. 14. Hexane absorption by polymethylene C_{1430} at different temperatures. Film no 5. Grams absorbed per gram polymethylene against saturation fraction.

- Δ 17°, series 7
 \square 22°, series 8

abscissa. This is in accordance with the view that only the amorphous parts of polymethylene absorb hexane. If C_{36} is heated above the melting point it too will absorb.

Judging from the hexane absorption the degree of crystallinity or orderliness seems to decrease from 100 % in the typical low molecular solid n -alkanes to a considerably lower value in C_{360} , which has still retained the brittle character. It is still lower in the tough elastical and strongly absorbing high polymers*. This is not surprising as the probability that the molecules orient themselves parallel to one another on solidification must decrease with increasing chain length. For the high polymers proper in Fig. 15 the observed absorption does not depend on the index in any simple way, obviously because the influence of chance deviations in crystallinity is of the same order of magnitude

* In a quite recent paper by Ueberreiter and Orthmann²⁴, this view is in principle supported by measurements of specific volumes of n -alkanes. The following "Ordnungsgrade" were observed at 20° C.

C_{28}	100 %
C_{35}	93 »
C_{45}	90 »
C_{65}	87 »
C_{110}	89 »
C_{1430}	88 »

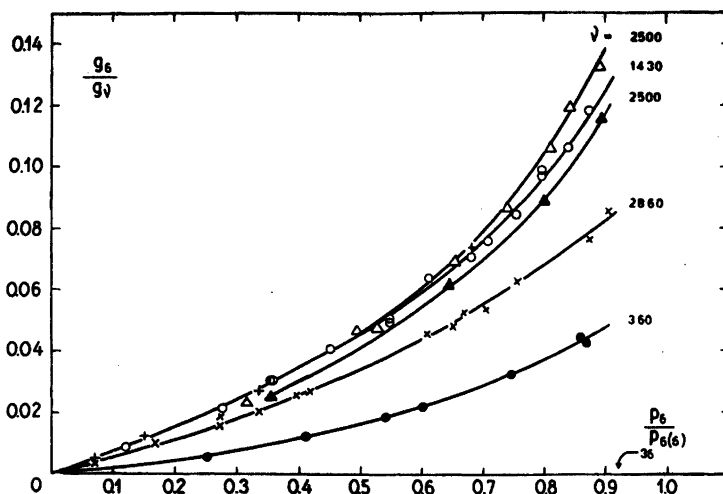


Fig. 15. Absorption of n-hexane by polymethylenes of different indices at 22°. Grams absorbed hexane per gram polymethylene against saturation fraction.

	ν	film no.	series
●	360	8	11
○	1 430	1	6
+	1 430	1	5
△	2 500	6	12
▲	2 500	7	13
×	2 860	10, 10b, 10d	4

as the influence of chain length, and the two effects may either oppose or fortify one another. It is perhaps worth noticing that the sequence of indices in Fig. 15 is the same as that observed in the solubility experiments on page 249. C_{1430} and C_{2500} dissolved in the concentration 5% in xylene at 75° C, whereas C_{360} and C_{2860} required 85° C.

As will be shown in a subsequent paper theoretical considerations indicate that in all probability the hexane absorption by amorphous polymethylene at constant temperature and vapour pressure is independent of the index of polymethylene, provided this is larger than 54. If so, the deviations of the curves in Fig. 15 have to be ascribed exclusively to deviations in crystallinity of the individual films. As previously mentioned the crystallinity probably decreases with increasing index for mechanical reasons, but this variation is overshadowed by chance deviations at least in the extremely high-index polymethylenes.

It follows that intercomparison of hexane absorption by solid polymethylenes is of little value, unless carried out at some well-defined degree of

crystallinity. Even above the "melting point", where the crystallinity should be zero, such comparison may be difficult, because there is evidence that a certain degree of orientation prevails even in the liquid state⁹.

Richards¹⁹ by measurements of the swelling of polymethylenes in liquid xylene observed an increasing absorption with decreasing index. 10% was absorbed by polymethylene of index 2 860 and about 20% by polymethylene of index *ca.* 700. Similar results were obtained with liquid *n*-hexane at 20°C^{19, p. 22}. Solid low index alkanes, however, do not absorb at all. Consequently, accepting Richards results, the absorption should pass a maximum at a certain index and then decrease. If this index lies somewhere between 360 and 1 400 then qualitative accordance is attained between our results and those of Richards, but in view of the uncertainties outlined above little or no importance can be attached to such comparisons.

K. The absorption of different volatile alkanes by polymethylene C₂₈₆₀ at constant temperature.

Fig. 16 illustrates the variation of the absorption with the index ν of the volatile alkane, the same polymethylene film (no. 10 d) having been used throughout. The temperature was 22°C. In order to permit direct comparison millimoles absorbed alkane per gram polymethylene is plotted against the saturation fraction. Hexane shows the larger absorption. For increasing index of normal alkanes the absorption decreases as expected. The effect of chain branching, judging from the data of "iso-octane" (8i), seems to be to lower the absorption relative to that of the normal compound, but obviously no general conclusion can be derived from this single experiment. The dotted parts of curve 8 and 8i are given with reserve, because the relevant data are close to the saturation point.

Richards^{19 p. 26, Table III} observed an increasing absorption (wt %) with increasing index up to a certain limit. The measurements were carried out at 20°C with liquid alkanes. Richards data are (symbols as elsewhere in this paper):

	ν_1	$\frac{g_{\nu_1}}{g_{\nu_2}}$	$\frac{g_{\nu_1}}{g_{\nu_1} \cdot M_{\nu_1}}$
<i>n</i> -pentane	5	0.06	0.0008
<i>n</i> -hexane	6	0.082	0.00095
<i>n</i> -heptane	7	0.105	0.00105

An extrapolation of the graphs in Fig. 16 to the saturation pressure is very uncertain, but it seems very unlikely that the absorption should vary with the index in opposite ways at saturation and at lower vapour pressures respectively.

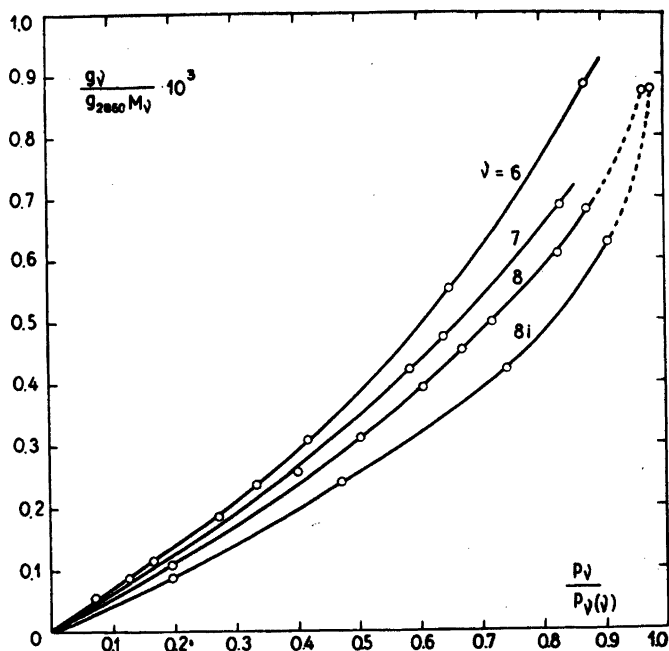


Fig. 16. Absorption of different volatile alkanes by polymethylene C_{2860} at 22° . Film no. 10d. Millimoles volatile alkane per gram polymethylene against saturation fraction.

ν	Volatile alkane	Series
6	n-hexane	4
7	n-heptane	14
8	n-octane	15
8	"iso-octane" (8i)	16

Even if the molecular weight is taken into account (last column in the above table) the sequence is the opposite to the one found by us for unsaturated vapours. In section L an indirect extrapolation is carried out. It confirmed the discrepancy.

The four series of data collected in Fig. 16 were measured in the sequence 6, 7, 8 and 8i. It is of course important to ensure, that no changes in structure have occurred during the measurements. As mentioned on page 259 there has not been found evidence of such changes at the relevant temperature. This point has been further confirmed by S. Brodersen (private communication), who re-measured the hexane absorption of the film no. 10 d at 22° and obtained data in complete agreement with those in Fig. 16 curve "6".

L. Mathematical representation of the results.

The isotherms in Fig. 12, 15 and 16 roughly give the concentration of the volatile alkane (v_1) in the swelled phase as a function of the vapour activity $p_{v_1}/p_{v_1(v_1)}$. For the present the deviation of the vapours from ideality will be neglected. Let a_{v_1} denote the activity and c_{v_1} the concentration in units of millimoles per gram polymethylene. It has been found that as a first approximation the equation

$$\frac{a_{v_1}}{c_{v_1}} = \alpha e^{\beta c_{v_1}} \quad (\text{I})$$

or in the logarithmic form

$$\log_{10} \frac{a_{v_1}}{c_{v_1}} = \log_{10} \alpha + 0.4343 \beta c_{v_1}, \quad (\text{II})$$

α and β being constants, is satisfied by the data, since all the curves in Fig. 12, 15 and 16 are transformed into straight lines when $\log \frac{a_{v_1}}{c_{v_1}}$ is plotted against c_{v_1} , as has been done in Fig. 17 and 18. The scatter is considerable at low values of c_{v_1} as should also be expected, because the relative accuracy of the underlying vapour pressure measurements is smaller in this region. For the significant data, however, the graphs leave no doubt about the linear relationship, except perhaps for octane (Fig. 17, 8), which displays a slight curvature. The numerical values of the slopes β and the intersections $\log \alpha$ have been graphically estimated. They are given in Table 5, column 7 and 6.

Table 5.

1	2	3	4	5	6	7	8	9	10	11
v_1	v_2	t	series no.	film no.	$\log \alpha$ (± 0.02)	β (± 0.05)	α (± 0.1)	c_{v_1} sat. vap.	$\left[\begin{array}{c} c_{v_1} \text{ vap.} \\ c_{v_1} \end{array} \right]_{c \rightarrow 0}$	$[c_{v_1}]_{s=1}$
6	360	22°	11	8	0.52	-1.31	3.3	0.00721	0.024	
6	1430	22°	5, 6	1	0.08	-0.46	1.2	721	0.009	
6	2500	22°	12	6	0.08	-0.51	1.2	721	0.009	
6	2500	22°	13	7	0.08	-0.44	1.2	721	0.009	
6	2860	22°	4	10, 10b, 10 d	0.18	-0.51	1.5	721	0.011	1.20
7	2860	22°	14	10 d	0.25	-0.58	1.8	214	0.004	1.00
8	2860	22°	15	10 d	0.30	-0.67	2.0	064	0.001	0.92
8 "i"	2860	22°	16	10 d	0.38	-0.81	2.4	233	0.006	0.77
6	1430	17°	2	1	0.08	-0.39	1.2	585	0.007	(1.8)
6	1430	27°	9	1	0.08	-0.48	1.2	881	0.011	

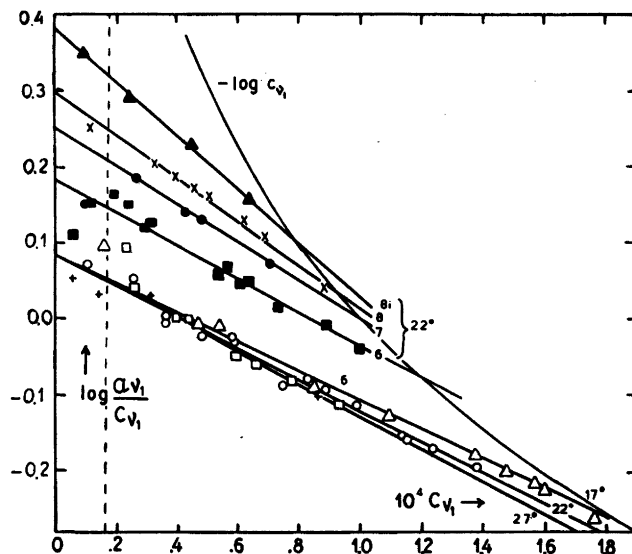


Fig. 17. Dependency of "activity coefficient" upon concentration. Transformation of the curves in Fig. 16 and 12.

Film no.	Series	Film no.	Series
■ 10, 10b, 10d	4	△ 1	2
● 10d	14	+ 1	5
× 10d	15	○ 1	6
▲ 10d	16	□ 1	9

The physical significance of α is realized in the following way. Let $c_{v_1 \text{ vap}}$ be the concentration of alkane vapours in units of millimoles per ml at a vapour pressure p_{v_1} and constant temperature. By $c_{v_1 \text{ sat. vap}}$ we denote the concentration of the saturated vapours, then, neglecting the small deviation from ideality, we have

$$a_{v_1} = \frac{c_{v_1 \text{ vap}}}{c_{v_1 \text{ sat. vap}}}$$

On substitution of this expression into (I) we obtain

$$\frac{c_{v_1 \text{ vap}}}{c_{v_1}} = \alpha \cdot c_{v_1 \text{ sat. vap}} \cdot e^{\beta c_{v_1}}$$

Hence $\alpha c_{v_1 \text{ sat. vap}}$ is the limiting distribution ratio of the volatile component between the vapour phase and the swelled phase for $c_{v_1} \rightarrow 0$. $c_{v_1 \text{ sat. vap}}$ is a constant, depending upon temperature, pressure and index of the alkane, its

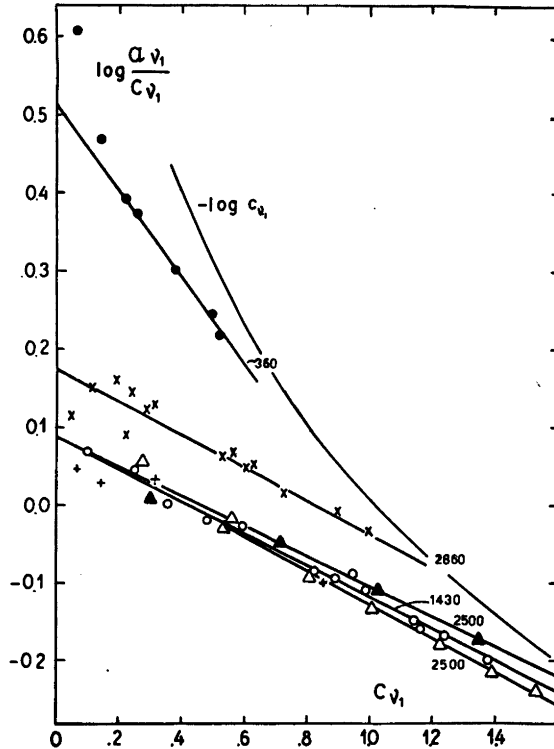


Fig. 18. Dependency of "activity coefficient" upon concentration. Transformation of the curves in Fig. 15 (same notation).

numerical values can be calculated from the saturation vapour pressures in Table 1 by means of the relation $p = RTc$. When p is given in units cm Hg and c in millimoles per ml, the equation becomes $c = p/62.37 T$, which has been used for calculation of the values of $c_{v_1 \text{ sat. vap}}$ given in column 9. Column 10 contains approximate values of the limiting distribution ratio, obtained as the product of a and $c_{v_1 \text{ sat. vap}}$. This calculation implies the approximation of regarding the unit *millimoles per gram* used for c_{v_1} equal to *millimoles per ml*. As, however, the density of polymethylenes is very close to 1 this is justified

for the present purpose. With this approximation the reciprocal values $\frac{c_{v_1}}{c_{v_1 \text{ vap. sat}}}$ are Ostwald's solubility coefficients.

In order to correlate in terms of solubility our vapour swelling data with those obtained by Richards (*vide* p. 267) for swelling in liquid alkanes the curves in Fig. 12, 15 and 16 should be extrapolated to unit activity $p_{v_1}/p_{v_1(v_1)}$

= 1, which is by definition the activity of the pure liquid. For this procedure the transformed isotherms in Fig. 17 and 18 are much more suitable. Inserting $a_{v_1} = 1$ into equation (II) we get

$$-\log c_{v_1} = \log a + 0.4343 \beta c_{v_1} \quad (\text{III})$$

Consequently the extrapolated values of c_{v_1} for $a_{v_1} = 1$ can be read directly on Fig. 17 as the abscissae of the intersection points between the function $-\log c_{v_1}$ and the respective straight lines. The solubilities obtained for the four different alkanes in polymethylene C_{2860} are listed in column 11. Their order of magnitude, 1 millimole per gram, agree quite well with Richard's solubilities of the liquid alkanes in a non-specified polymethylene sample at 20°, but the sequence is the opposite to that observed by Richards.

The intersections are only well-defined for C_{2860} , whereas the lines of C_{2500} and C_{1430} are approached almost asymptotically by the $-\log c$ curve (Fig. 18). For C_{360} there appears to be no intersection at all, which might be indicative of unlimited solubility at room temperature. Although this is true of the low-molecular linear "polymethylenes" up to about C_{16} it is against experimental evidence in the region of solid high polymers. It is probable, therefore, that the non-existence of intersection for C_{360} rather indicates that the equation (II) is a less good approximation at lower indices, and that the curvature suggested by the two points off the line is in fact real. By extrapolation of the C_{360} graph in Fig. 15 to $p_6/p_{6(6)} = 1$ we get $g_6/g_{6(6)} \approx 0.06$ corresponding to an intersection in Fig. 18 at $c = 0.07$.

The bearing of the swelling experiments described in this paper on the theory of congruency will be discussed in a subsequent paper.

The author is greatly indebted to the late professor J. N. Brønsted for suggesting the investigation and for inspiring criticism. My thanks are due to prof. dr. J. A. Christiansen, civiling. A. E. Lansner and mag. scient. Jørgen Koefoed for discussion.

REFERENCES

1. Brønsted, J. N., and Koefoed, J. *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **22** (1946) no. 17.
2. Fox, J. J., and Martin, A. E. *Proc. Roy. Soc. A* **175** (1940) 226.
3. Bunn, C. W. *Trans. Faraday Soc.* **35** (1939) 482.
4. Müller, A. *Proc. Roy. Soc. A* **120** (1928) 437.
5. Mark, H., and Meyer, K. H. *Z. physik. Chem.* **B 2** (1929) 115.
6. Bunn, C. W., and Alcock, T. C. *Trans. Faraday Soc.* **41** (1945) 317.
7. Huggins, M. L. *J. Chem. Phys.* **13** (1945) 37.
8. Hunter, E., and Oakes, W. G. *Trans. Faraday Soc.* **41** (1945) 49.
9. Raine, H. C., Richards, R. B., and Ryder, H. *Trans. Faraday Soc.* **41** (1945) 56.

10. Charlesby, A. *Trans. Faraday Soc.* **38** (1942) 320.
11. Richards, R. B. *Trans. Faraday Soc.* **41** (1945) 127.
12. Richards, R. B. *Trans. Faraday Soc.* **42** (1946) 22.
13. Klit, A. *Fraktioneret Destillation*, København, 1943.
14. Timmermans, J., and Martin, F. *J. chim. phys.* **25** (1928) 412.
15. Egloff, G. *Physical Constants of Hydrocarbons*, New York, 1939.
16. Edgar, G. *Ind. Eng. Chem.* **19** (1927) 146.
17. Brodersen, S. *Private communication*.
18. Brønsted, J. N., and Volquartz, K. *Trans. Faraday Soc.* **35** (1939) 578.
19. Richards, R. B. *Trans. Faraday Soc.* **42** (1946) 18, Table IV.
20. Huggins, M. L. *J. Phys. Chem.* **46** (1942) 151.
21. Flory, P. J. *J. Chem. Phys.* **10** (1942) 51.
22. Staudinger, H. *Organische Kolloidchemie*, Braunschweig 1950, p. 208.
23. Kuhn, W. *Z. angew. Chem.* **49** (1936) 858.
24. Ueberreiter, K., and Orthmann, K.-J.. *Kolloid Z.* **128** (1952) 125.

Received November 26, 1952.