

A Study on Contraction, Relative Viscosity and Melting Curves of Some Glass-forming Hydrocarbon Mixtures

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The contraction, relative viscosity and melting curves have been studied for a number of hydrocarbon mixtures that form glassy states upon freezing at 77°K. The commonly used isopentane — 3-methyl pentane glasses as well as three new mixtures have been studied.

During the course of an investigation of the photolysis of organic substances in a rigid matrix at liquid nitrogen temperature it was felt desirable to study, quantitatively, the following properties of the different glass-forming mixtures: the specific volume ratio between 298° and 77°K, the rigidity of the matrix as a function of temperature, and the melting behaviour of the matrix. The contraction of the mixture must be known in order to convert concentration values from room temperature to 77°K. The viscosity of the matrix has a marked influence upon the photolysis path^{1, 2} but has, so far, not been quantitatively estimated as a function of temperature. Finally, the heating curve of a particular matrix mixture reveals the possible existence of microcrystalline structures in the glass at 77°K or the formation of crystals during warm-up.

The following glass-forming mixtures have been studied (volume ratios are given):

3-Methyl pentane (pure)¹

Isopentane — 3-methyl pentane (6:1)³

Isopentane — 3-methyl pentane (2:3)¹

Pentane — neo-hexane (3:8)⁴

3-Methyl pentane — methyl cyclohexane (1:2)⁴

3-Methyl pentane — methyl cyclohexane (1:6)⁴

MATERIALS

All hydrocarbons were Phillips Petroleum Company "pure" grade hydrocarbons, except isopentane and 3-methyl pentane, which were "technical" grade samples from the

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same company. They were all purified by a routine method, which, in principle, is described in the literature ⁵.

After the hydrocarbon (about 2 l) had been treated with concentrated sulphuric acid for 5 h, it was neutralized, washed with water and dried over night with "Drierite". The liquid was refluxed over sodium wire, transferred to a still pot, freshly prepared sodium wire was added and the sample was carefully distilled in a 35 plate all glass column packed with Fenske helices; reflux ratio 1:30, 150–200 ml being collected every 24 h. From these fractions samples were withdrawn and analyzed on a gas chromatograph (Pye Argon Chromatograph Type 12000) with dioctyl phthalate as stationary phase. For pentane and neo-hexane all fractions which contained more than 0.05 % impurities were discarded, for cyclohexane the corresponding figure was 0.1 %. *i*-Pentane was allowed to contain max. 0.5 % pentane and for 3-methyl pentane max. 1 % 2-methyl pentane was allowed.

Samples from those fractions which passed the gas chromatographic analysis were tested for ultraviolet transmission below 50 kc. cm^{-1} in a spectrophotometer (Beckman DU equipped with a photomultiplier), and fractions exhibiting a transmission appreciable lower than the pure compound were recycled.

The pure fractions were brought together and allowed to pass a glass column (60 \times 2.5 cm) packed with Davidson No. 200 mesh silica gel. The silica gel had been activated in the tube at 350°C. In order to remove the last traces of water, the silica gel tube was evacuated to 1 mm of Hg at 350° and then allowed to cool in vacuum. After the silica gel treatment the ultraviolet transmission was checked again. It was found that a second treatment with fresh silica gel did not improve the spectrum. During all manipulations every precaution was taken to prevent moisture from entering the liquids.

CONTRACTION

Precise quantitative measurements of the contraction which occurs when organic matrix solutions are cooled in liquid nitrogen have been reported for a few hydrocarbons, mainly mixtures of isopentane and methyl cyclohexane ⁶. Average values given elsewhere are said to be valid for several different mixtures ^{1, 3}.

A pear-shaped flask (27 ml) was melted on to a 10 ml precision burette equipped with a standard joint. A movable electrical heater, length 5 cm, was wound around the burette and the apparatus was accurately calibrated by weighing. When the hydrocarbon mixture had been poured into the apparatus, the system was out-gassed and closed by means of a stop-cock attached to the burette by means of a standard joint. The volume of the liquid was measured at 293°K in a thermostat and the apparatus was then transferred to a Dewar vessel with liquid nitrogen where it was cooled very slowly. The heater was used to avoid the formation of a deep meniscus in the narrow burette tube. When the volume measurements were made, all portions of the hydrocarbon solutions were in the liquid nitrogen. All mixtures were repeatedly cycled between room temperature and liquid nitrogen, and the measurements were repeated with a second apparatus. The results are given in Table 1.

Table 1. Ratio of specific volume at 77°K and 293°K. The uncertainties are expressed as mean deviations.

Hydrocarbons	$V_{77^\circ\text{K}}/V_{293^\circ\text{K}}$
Isopentane — 3-methyl pentane (6:1)	0.7605 ± 0.0004
Isopentane — 3-methyl pentane (2:3)	0.7713 ± 0.0004
3-methyl pentane (pure)	0.7845 ± 0.0006
Pentane — neo-hexane (3:8)	0.7694 ± 0.0005

RELATIVE VISCOSITY

The rigidity of a number of hydrocarbon mixtures has been reported in very general terms^{1, 3, 7}. Quantitative viscosity comparisons between different mixtures have not been performed as judged from what has been published. A study was therefore undertaken to compare the temperature ranges in which different mixtures start to become fluid. The velocity of fall of a ball-shaped body was taken as a measure of the viscosity.

A cylindrically shaped copper block wound with a heating wire (8×5 cm) was placed in the bottom of a Dewar vessel (45×5.6 cm); it was thermally insulated from the inner wall of the Dewar by means of thin cork rings. Two holes, both 6 cm deep, were drilled in the block, one centrally, diameter 1.7 cm, the second, diameter 0.6 cm, close to the first one. A small third hole near the edge of the block carried a glass tube from the outside of the Dewar to its bottom. A cylindrical glass vessel (diam. 1.6 cm) provided with a 40 cm long stem (diam. 0.8 cm) could be inserted in the central hole, and a brass ring fastened to the stem served as a lid for the central cavity. Inside the stem a thin rod (35×0.3 cm) made from balsa wood could be moved up and down; it was guided by two small rings of steel placed 25 cm apart on the rod. The lower end of the rod was provided with a stainless steel ball (diam. 0.632 cm), the total weight of the movable part being 2.85 g. The temperature inside the copper block could be measured by means of a platinum resistance thermometer (Type Heraeus BS5) placed in the 0.6 cm hole. The dimensions of the coil were 1.2×0.5 cm and its resistance at 273°K was 100 Ω . The thermometer was used in connection with a Mueller G 1 bridge (Type Rubicon 1551), and it was calibrated in liquid oxygen, solid carbon dioxide, ice-water and steam.

The hydrocarbon mixture was poured into the glass vessel until it nearly reached the stem. The falling body was inserted and kept in the upper part of the stem by means of a small magnet outside the tube. The liquid was outgassed and the vessel was closed with a stop-cock attached to the stem by means of a standard joint. Liquid nitrogen was poured into the Dewar until the copper block was surrounded with the liquid, while the glass tube with the hydrocarbons was slowly pre-cooled in another Dewar. Great care was taken to prevent the surface of the glassy mixture from forming a deep meniscus.

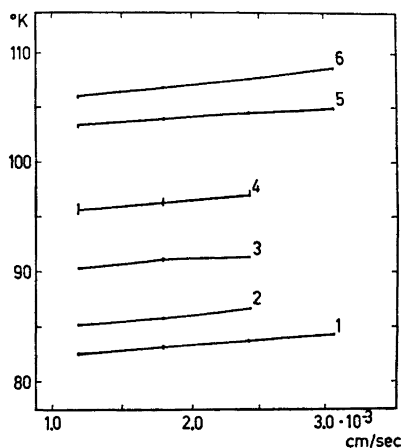


Fig. 1. Relative viscosity for different matrices. (1) *i*-pentane — 3-methyl pentane 6:1, (2) pentane — neo-hexane 3:8, (3) *i*-pentane — 3-methyl pentane 2:3, (4) pure 3-methyl pentane, (5) 3-methyl pentane — methyl cyclohexane 1:2 and (6) 3-methyl pentane — methyl cyclohexane 1:6.

The hydrocarbon mixture was placed in the copper block and allowed to reach liquid nitrogen temperature. The nitrogen was sucked off and the magnet was removed so that the stainless steel ball rested on the hard upper surface of the glass. When the heater was turned on, 1 watt produced a temperature increase of 0.2° per min. The position of the upper end of the balsa rod was measured and, together with the temperature, plotted against time. When the glass softened, the balsa rod started to move at a rate that was directly found from the plotted curve. Obviously, the slope of the curve represents the velocity of fall. Temperatures corresponding to slopes of 10° , 15° , 20° and 25° were evaluated. At least three independent runs were made for each hydrocarbon mixture. The surprisingly good reproducibility is shown in Fig. 1, in which the temperature is plotted against the velocity of fall for a number of hydrocarbons. The vertical extent of the markings represents the maximum deviation between various runs. A few experiments where the temperature rise was 1° per min gave exactly the same result.

According to Stokes Law the viscosity is a linear function of the velocity of fall. Although in this case the contact surface between the falling body and the substance is not constant during a run, the experiment can be used to arrange the hydrocarbon glasses in order of increasing rigidity (Fig. 1). It is of interest to note that the glasses numbered 5 and 6 are of higher viscosity than 3-methyl pentane. Both are mixtures of methyl cyclohexane and 3-methyl pentane, 2:1 and 6:1, respectively, and have not been used previously. However, they tend to crack when stored for several hours at 77°K , which somewhat limits their use.

MELTING CURVES

If the spectral behaviour of a matrix containing trapped unstable species is to be studied as a function of temperature, it is of importance that the specific heat in the melting region does not show any abrupt change. Therefore, the mixtures previously described were studied in a simple specific heat calorimeter.

A cylindrical glass vessel, diam. 3 cm, of 45 ml volume was equipped with an interior heater consisting of a manganin wire wound on a piece of glass tubing, that had been concentrically sealed into the vessel. The vessel was provided with a long stem through which a Heraeus BS5 platinum resistance thermometer could be inserted. The stem was equipped with five circular, highly polished, thin copper discs, equally spaced, serving as heat shields. The vessel fitted into a long, narrow glass Dewar.

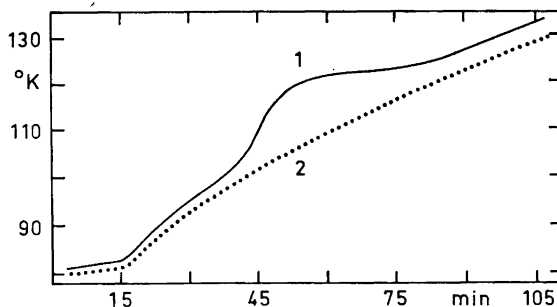


Fig. 2. Melting curves for (1) pentane — neo-hexane 3:8 and (2) isopentane — 3-methyl pentane 6:1.

The glass vessel was filled with the hydrocarbon mixture, the thermometer was inserted and the apparatus was outgassed and closed. The hydrocarbon mixture was cooled to 77°K in the Dewar and when this temperature was reached, the liquid nitrogen was removed. The system was then allowed to attain thermal equilibrium, a steady increase in temperature of about 0.1° per min was reached within 15 min. When 0.5 watt was supplied through the heater, the temperature increased at a rate of about 1° per min (Fig. 2). Although the resistance of the heating wire changed, the power was supplied at a constant rate by means of a circuit described elsewhere⁸.

3-Methyl pentane (pure) and isopentane — 3-methyl pentane (6:1 and 2:3) showed an evenly increasing specific heat according to curve 2. Curve 1 represents a typical rum with pentane — neo-hexane (3:8). At about 100°K crystallization started and the crystals melted at 121.9—122.2°K. Beyond 122°, the curve was found to be a direct extension of the curve below 100°K. The same eutecticum was found with varying composition of the glass and it represents neither of the pure components (pentane m.p. 141.7, neo-hexane m.p. 175.0°K). The practical use of the mixture as a matrix is by no means disturbed by the crystallization, which starts at a temperature well above the melting region. Furthermore, crystallization has never been observed during freezing.

The very smooth curves obtained for the isopentane — 3-methyl pentane glasses studied conclusively prove the absence of a microcrystalline structure, which might undergo phase transformation below 150°K.

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