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Diblock semifluorinated n-alkanes purification by gel phase formation in organic solvents: $C_8F_{17}C_{18}H_{37}$ in alcohols

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Abstract

The formation of a gel-like phase observed with some diblock semifluorinated n-alkanes dissolved in organic solvents was investigated as a purification method for these compounds. Experiments were carried out with $F(CF_2)_8(CH_2)_{18}H$ by using absolute ethanol or methanol as solvent. Starting from samples with different initial degrees of purity, and using a very strict methodology, the amount of solvent giving the highest yield of purification was determined. The different solubilizing power of the solvents used did not greatly influenced the purification process. Different cooling rates were also investigated, but only small influences on the treatment effectiveness were observed. © 1997 Elsevier Science S.A.

Keywords: Diblock semifluorinated n-alkanes; Gel phase; Purification method

1. Introduction

Diblock semifluorinated n-alkanes $F(CF_2)_n(CH_2)_mH$ are a family of fluorinated compounds extensively studied in recent years in relation to their interesting peculiarities [1]. In particular, the formation of a gel-like phase has been observed when a solution of some of them in an organic solvent is cooled to ambient temperature [2–4]. The correlation between concentration of the fluorinated compound in the mixture and the temperature at which the phenomenon occurs [3], as well as between cooling rate and gel phase structure [5], have been suitably evidenced. But nothing else has been reported about this particular behaviour of these compounds.

The structure of tightly interlaced crystallites proposed for this gel phase [5] suggests the possibility of testing this process as a purification method for semifluorinated n-alkanes. These compounds are usually prepared by a two-step procedure (see Ref. [1] and references cited therein) which leads to a number of by-products depending on the adopted experimental conditions. Also, in view of some critical uses proposed for them [6–8], the presence of by-products has to be avoided. By formation of the gel phase an increase of the purity degree can be expected, just as in the normal process of crystallization.

Starting from these considerations, a study was accomplished in order to verify the possibility of purifying semifluorinated n-alkanes by this method and to acquire further information on the behaviour of these semifluorinated compounds in organic solvents. The experimental results are reported and discussed below.

2. Experimental

2.1. Materials

$F(CF_2)_8(CH_2)_{18}H$ was the semifluorinated n-alkane employed in the experiments. It was synthesized according to the usual free-radical initiated addition of perfluoro-n-alkyl iodides to 1-olefins, followed by reductive dehydroiodination with Zn and hydrogen chloride. In order to obtain a sample suitable for the purpose of this work, i.e. not too pure, a non-careful procedure was adopted, especially in the second step. A representative experiment is given here.

54.6 g (0.10 moles) of $C_8F_{17}I$ (Hoescht, 97% pure), 12.6 g (0.05 moles) of $C_{18}H_{36}$ (Aldrich, 90% pure) and 1.0 g (0.006 moles) of AIBN (Jansenn, 98% pure) were placed in a 250 ml stainless steel vessel equipped with a condenser, repeatedly purged with nitrogen and heated at 80 °C for 4 h. The colorless reaction mixture (66.8 g) was distilled at reduced pressure in order to recover the unreacted reagents. The residue (40.0 g), dissolved in 100 ml of ethanol, was dropped under vigorous mechanical stirring into a 1 l four-

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necked round-bottom glass vessel equipped with separatory funnels, a mechanical stirrer and a condenser, containing 7 g of Zn powder and 200 ml of ethanol, and brought to a gentle boil; 15 ml of 36% aqueous HCl were simultaneously and suitably dropped in to assure a vigorous foaming. After all the zinc had been consumed, the reaction mixture was cooled to room temperature and the solidified organic phase was recovered, washed with hot water, dried on sodium sulfate and analyzed. The GLC percentage determined for $C_8F_{17}C_{18}H_{37}$ was on average about 70%.

The treatments planned for this study were accomplished by using absolute ethanol (Prolabo, 99,8% pure) or methanol (C. Erba, 99,9% pure) as solvent.

2.2. Methodology

Since the gel-phase formation is sensitive to various parameters, the phenomenon was studied under strictly controlled conditions, particularly as regards the cooling rate. So a water bath maintained at 20 °C was employed for all the experiments, and the same volume of solvent (250 ml) was always used, in which different sample amounts were dissolved in order to operate with different values of millilitres of solvent to grams of sample (ml g^{-1}), the dilution ratio. The following procedure was adopted in all the experiments.

A weighed sample of the semifluorinated compound was placed in a 400 ml pyrex vessel together with 250 ml of solvent and the resultant mixture was brought to a gentle boil under vigorous magnetic stirring. In this manner, the complete dissolution of the sample was generally accomplished, except for some experiments carried out with methanol as solvent. The vessel was then suddenly transferred to the water bath maintained at 20 °C and allowed quietly to cool; the inside temperature was followed in time by a thermometer placed in the centre with the bulb 1 cm from the bottom. During the cooling the gel phase began to form at a temperature depending either on the initial purity degree of the sample or on the dilution ratio; this "gel point" could be easily observed since the temperature remained unchanged for some time. When the thermometer registered 20 °C, the gel phase was recovered by filtration under vacuum, removing the liquid phase as far as possible; the residue was then oven-dried at 40 °C, weighed and analyzed.

2.3. GLC analysis

The purity increase of the samples was followed by using the GLC technique. The sample, dissolved in diethyl ether (1:10 v/v), was analysed by a Perkin-Elmer Sigma 3 gas chromatograph (1 m × 2 mm stainless column filled with OV 101, 150 °C for 5 min, then 3 °C min^{-1} to 260 °C, 20 cm^3 min^{-1} of He as the gas carrier, flame ionization detector), equipped with a Perkin–Elmer Sigma 1 system for the quantitative determinations.

3. Results and discussion

Preliminary experiments of solubility had pointed out a greater solubility of $C_8F_{17}C_{18}H_{36}$ in ethanol compared with methanol. Then, the experiments were carried out by using each of these solvents in order to emphasize possible different behaviours.

3.1. Experiments with ethanol

3.1.1. Cooling rate

As mentioned above, the cooling rate can have some influence on the gel phase formation; it should be then indispensable that this parameter was the same for all the experiments. But determination in time of the bulk temperature demonstrated that the cooling rate, defined as the time required for the solution to arrive at the bath temperature, generally depends on either the initial purity degree of the sample or the dilution ratio. This influence resulted in particularly marked high values of the dilution rate and low values of the initial purity degree of the sample.

The initial cooling rate was then taken as a reference; this parameter remained rather constant, and a mean value of 38.3 ± 3 °C min^{-1} was determined for all the treatments on the basis of the first minute of cooling.

3.1.2. Gel-point determination

In each experiment the bulk temperature was continuously checked and the registered values plotted versus time gave the profile shown in Fig. 1 as an example. As can be seen, the gel-point can be easily determined from these figures as temperature remains almost unchanged in time during the gel-phase formation. The observed gel-points increase either with the initial purity degree or the dilution ratio, as shown in Fig. 2.

3.1.3. Gel phase formation

Within the framework of these experiments both the quantitative and qualitative aspects were separately considered in each treatment, i.e. the recovered amount of sample and its

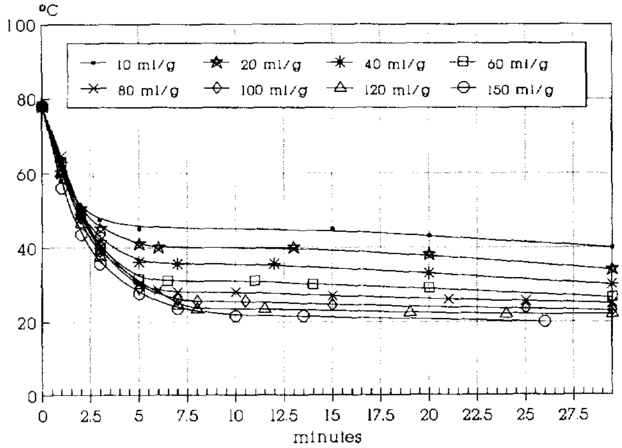

Fig. 1. Gel points determined for $C_8F_{17}C_{18}H_{37}$ in ethanol (initial purity degree, 65%).

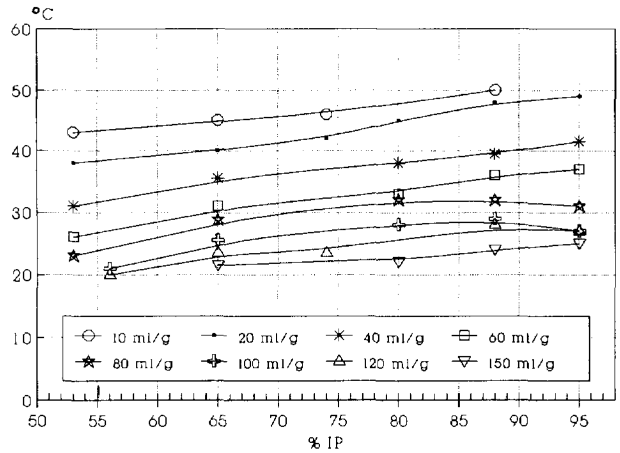

Fig. 2. Gel points of $C_8F_{17}C_{18}H_{37}$ in ethanol versus initial purity degrees at different dilution ratios.

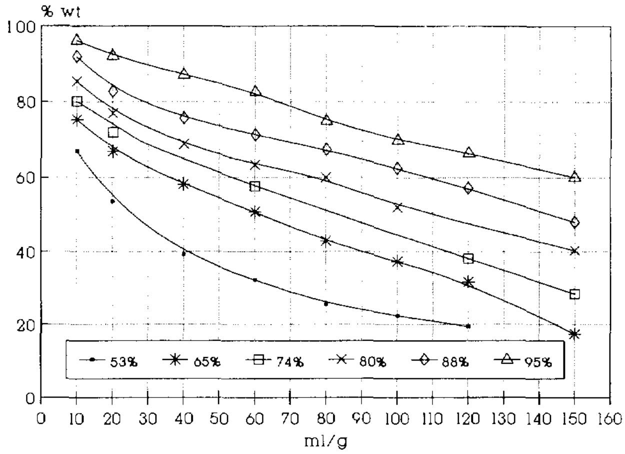

Fig. 3. Percent recovered amount versus dilution ratio at different initial purity degrees for $C_8F_{17}C_{18}H_{37}$ in ethanol.

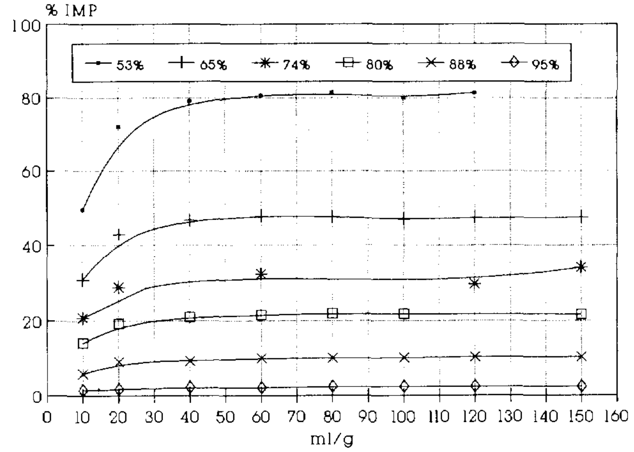

Fig. 4. Percent purity improvement versus dilution ratio at different initial purity degrees for $C_8F_{17}C_{18}H_{37}$ in ethanol.

purity improvement. In Fig. 3 the percentage recovered amount with respect to the treated amount of sample (%wt) is reported against the dilution ratio at different initial purity degrees (%IP): as it can be seen, %wt increases with %IP and decreases as the dilution ratio increases. In Fig. 4 the percent purity improvement (%IMP) with respect the initial purity degree of the treated sample is reported versus the dilution ratio: %IMP results in being strongly sensitive to %IP, but does not greatly depend on the dilution ratio. In particular, beyond 60 ml g^{-1} small changes of %IMP can be observed in any case.

For an overall evaluation of the effectiveness of the treatment (yield) both these parameters were considered as follows:

$$Y\,(\text{yield}) = [(\%\text{wt}) \times (\%\text{IMP})]/100 \qquad (1)$$

By plotting the values of Y in this manner, calculated versus the dilution ratio, the diagram of Fig. 5 was obtained, in which it must be pointed out that curves present a maximum, which is more evident for the lowest values of %IP. These maximum values plotted versus %IP led to the diagram of Fig. 6, where the dilution ratio giving the highest yield can be read for any initial purity degree of the sample to be treated.

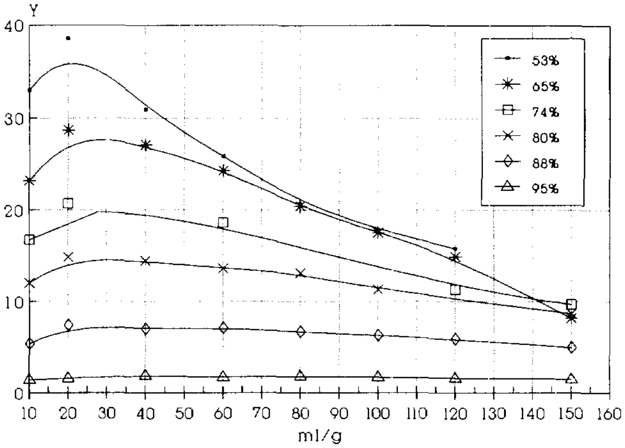

Fig. 5. Treatment yield versus dilution ratio at different initial purity degrees for $C_8F_{17}C_{18}H_{37}$ in ethanol.

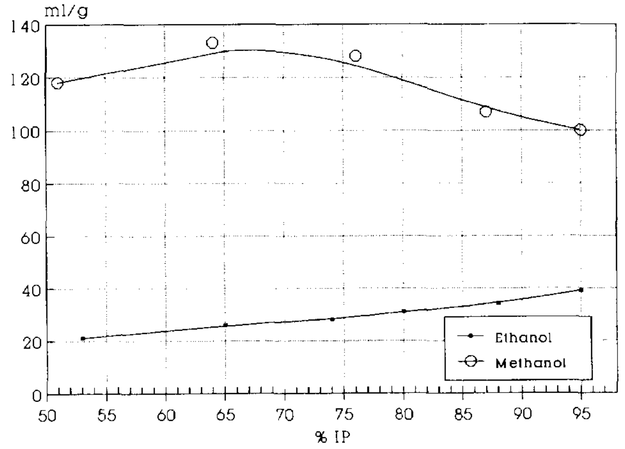

Fig. 6. Dilution ratio giving the highest yield versus initial purity degree for $C_8F_{17}C_{18}H_{37}$ in ethanol and methanol.

3.2. Experiments with methanol

3.2.1. Mean initial cooling rate

In this case the mean initial cooling rate, determined as mentioned above, was 30.2 °C min^{-1}, slightly lower than that determined for ethanol. This, however, has no relevant influence on the gel phase formation (see below).

3.2.2. Gel point determination

Fig. 7 shows the change of temperature versus time observed in the experiments carried out using methanol as solvent. In comparison with ethanol a less regular behaviour can be observed, also on varying the dilution ratio; determination of the gel point was then less precise in this case. Curves of gel point versus initial purity degree of the sample maintained the same profile shown for ethanol in Fig. 2, whereas differences can be seen in Fig. 8 where the profiles versus the dilution ratio are compared. This last behaviour could be ascribed to the lower solubilizing power of methanol, whose solutions are almost always saturated. In fact, especially for high values of %IP and low dilution ratios, non-complete dissolution of the sample was often observed.

3.2.3. Gel phase formation

In Fig. 9 the percent recovered amount of the treated sample is reported versus the dilution ratio at different initial purity degrees. As can be seen, curves have a remarkably different profile with respect to those observed with ethanol; in particular, they first increase with the dilution ratio, then remain almost constant and finally decrease with the same profile observed with ethanol. Also this behaviour can be clearly ascribed to the lower solubilizing power of methanol; in fact, at the beginning, %wt increases with the dilution ratio for the greater amounts of sample dissolved, whereas under very dilute conditions it decreases for the opposite reason.

From the extrapolation of these experimental data it was possible to define the solubility limit corresponding to each initial purity degree. These values are shown in Fig. 10 together with the analogues values determined with ethanol. As can be seen, for any sample the amount of solvent required for its complete solubilization is less for ethanol than for methanol. This difference, however, became smaller and smaller as the initial purity degree of the sample increases.

Fig. 11 shows as the observed percent purity improvement changes with the dilution ratio; as can be seen, changes are

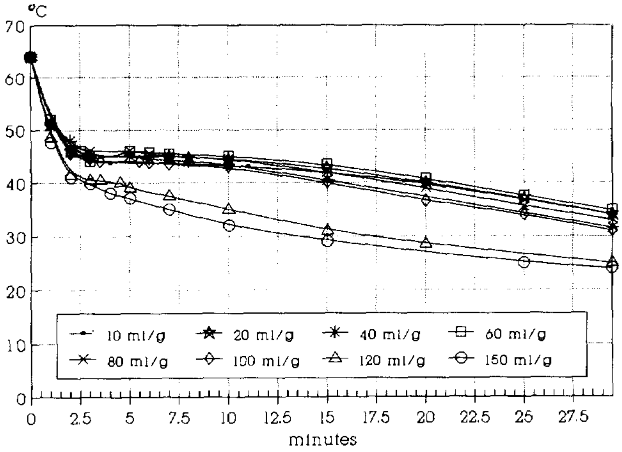

Fig. 7. Gel points determined for $C_8F_{17}C_{18}H_{37}$ in methanol (initial purity degree, 64%).

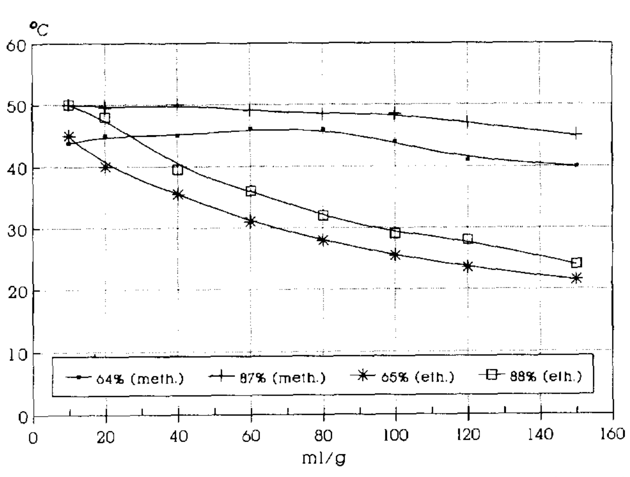

Fig. 8. Comparison between gel point versus dilution ratio profiles at the stated initial purity degrees for $C_8F_{17}C_{18}H_{37}$ in ethanol and methanol.

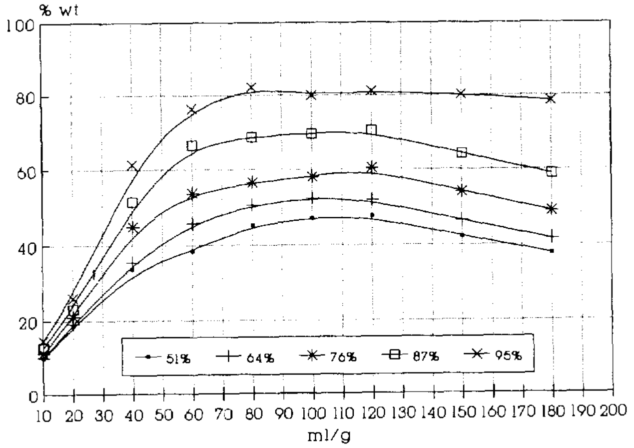

Fig. 9. Percent recovered amount versus dilution ratio at different initial purity degrees for $C_8F_{17}C_{18}H_{37}$ in methanol.

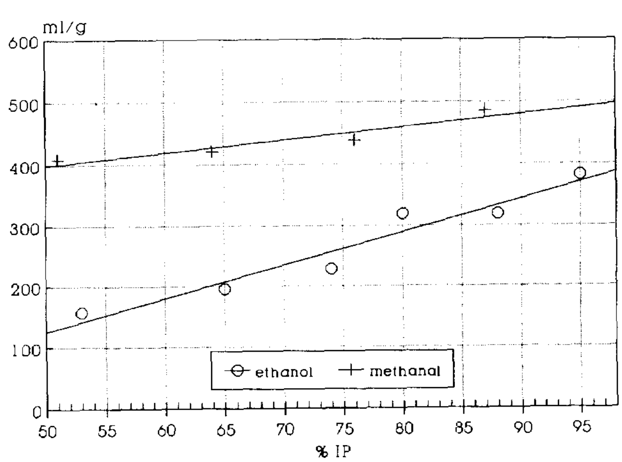

Fig. 10. Solubility limits in ethanol and methanol for samples of $C_8F_{17}C_{18}H_{37}$ having any initial purity degree.

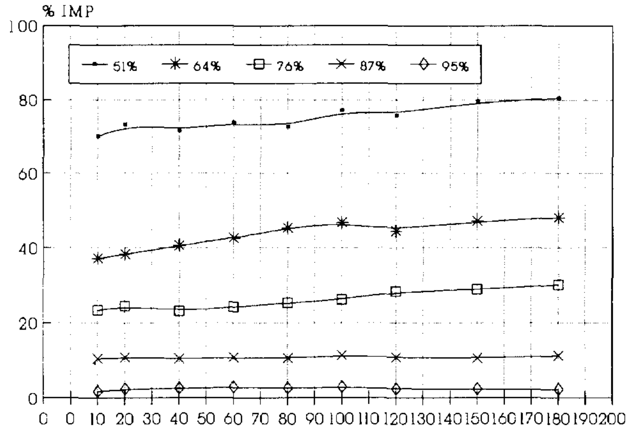

Fig. 11. Percent purity improvement versus dilution ratio at different initial purity degrees for $C_8F_{17}C_{18}H_{37}$ in methanol.

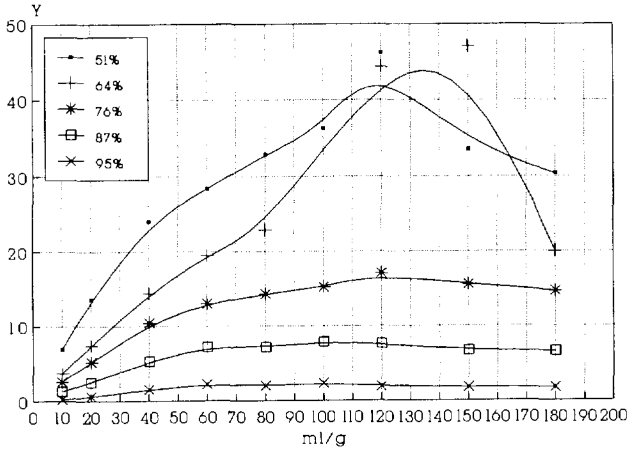

Fig. 12. Treatment yield versus dilution ratio at different initial purity degrees for $C_8F_{17}C_{18}H_{37}$ in methanol.

very little. The corresponding values of Y, calculated by Ref. [1], are shown in Fig. 12: also in this case well marked maxima can be seen, especially for low values of the initial purity degree. The maximum values plotted versus %IP gave the curve reported in Fig. 6 for comparison with that obtained with ethanol. An almost independence from the initial purity degree of the sample can so be observed, contrary to what can be seen with ethanol.

3.3. Influence of the cooling rate

Additional experiments were carried out in order to evaluate how a different cooling rate could influence the gel phase formation. A reduction of the cooling rate could reasonably lead to an amelioration particularly of the percent purity improvement, and then of the treatment yield. Thus, 12.5 g of samples with different initial purity degrees were treated with 250 ml of ethanol at a constant dilution rate of 20 ml g^{-1}. The mixtures were then heated to the boiling point (78 °C) and put into a water bath at 75 °C. Then bath was allowed to spontaneously cool to room temperature (20 °C); the determined initial cooling rate was in this case 4.2 °C min^{-1}, well below that found in the experiments carried out in the bath at 20 °C. Results are detailed in Fig. 13, where the corresponding values of the experiments accomplished at the higher cooling rate are also reported for comparison. As can be seen, a lower cooling rate does not bring significant differences with regard to the considered parameters.

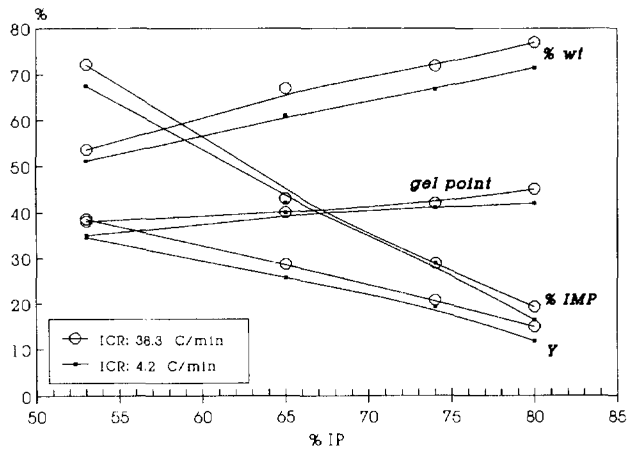

Fig. 13. Comparison between experiments carried out at different initial cooling rate (ICR) with a dilution ratio of 20 ml g^{-1}.

4. Conclusions

The experiments whose results were reported and discussed above show that diblock semifluorinated n-alkanes can be purified by gel phase formation. The yield of these purification treatments fundamentally depends on the solvent, the dilution ratio adopted and the initial purity degree of the sample. In particular, the dilution ratio giving the highest yield for any value of the initial purity degree was determined.

With regard to the solvent to be used, the experimental results show that its greater or smaller solubilizing power towards these semifluorinated compounds does not greatly influence the effectiveness of their purification. But solvents with higher solubilizing power (such as ethanol) allow one to obtain comparable results by using smaller amounts of solvent.

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