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Synthesis of $F(CF_2)_8(CH_2)_8H$ and gel phase formation from its solutions in homologous alcohols

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Abstract

The behavior of $F(CF_2)_8(CH_2)_8H$ in methanol, ethanol and propanol with reference to the gel phase formation of diblock semifluorinated *n*-alkanes was investigated. Samples with different degrees of purity employing different volumes of solvent were studied in order to ascertain the influence of the process variables on the gel phase formation. For each alcohol the volume leading to the best result was determined and the relative values were compared in order to evaluate the effectiveness of this treatment as a purification method for these semifluorinated compounds. The synthesis of $F(CF_2)_8(CH_2)_8H$ was also studied with reference to the influence of ratio of reactants and temperature on the addition of the fluorinated reactant to the 1-olefin. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Diblock semifluorinated *n*-alkanes; Gel phase; Purification method; Perfluoroalkyl iodides addition; $F(CF_2)_8(CH_2)_8H$

1. Introduction

Diblock semifluorinated *n*-alkanes $F(CF_2)_n(CH_2)_mH$ were studied in recent years in relation to their interesting peculiarities (see [1] and references cited therein). Particular applications were suggested for these semifluorinated compounds, especially within the biomedical field, either as interfacial active compounds or as oxygen carriers [2–4]. As these critical uses require high degrees of purity, a purification method of the crude compounds by means of the gel phase that these semifluorinated *n*-alkanes form when their solution in an organic solvent is cooled to ambient temperature [5–7] was studied.

In previous work [8], the behavior of $F(CF_2)_8(CH_2)_{18}H$ in methanol and ethanol was studied paying particular attention to the gel phase formation. Because of the many parameters that influence the gel phase formation a procedure under strict conditions was employed in order to exploit this process as a purification method. This procedure was adopted to ascertain the behavior of $F(CF_2)_8(CH_2)_8H$ in three homologous alcohols (methanol, ethanol and propanol) with respect to the formation of the gel phase. For each alcohol a series of treatments was performed using samples of the semifluorinated compound with different purity and varying the volume of solvent used, in order to define the dilution ratio (DR) (milliliter of solvent per gram of sample) leading to the best result in purification. However, $F(CF_2)_8(CH_2)_8H$ differs from $F(CF_2)_8(CH_2)_{18}H$ because its hydrogenated fragment is shorter thus influencing its melting point. Crude $F(CF_2)_8(CH_2)_8H$ melts at about 18°C (or below depending on its degree of purity). The previously determined procedure thus had to be modified by cooling the solutions down to -15°C.

Prior to these experiments on the gel phase formation, a study on the first step of the reaction leading to the intermediate $F(CF_2)_8\text{–}CH_2\text{–}CHI\text{–}(CH_2)_6H$ was performed under different conditions of ratio of reactants and temperature in order to define their influence on the extent of its formation.

2. Results and discussion

2.1. Addition of perfluorooctyl iodide to 1-octene

The study on the reaction leading to the formation of $F(CF_2)_8(CH_2)_8H$ was limited to the first step which is more sensitive than the second one to changes in operational conditions. The ratio of reactants used and the temperature were varied whilst the same ratio of azobis-*iso*-butyronitrile (AIBN) to the limiting reactant (LR) was used in each case. Three series of experiments were carried out at 60, 80 and

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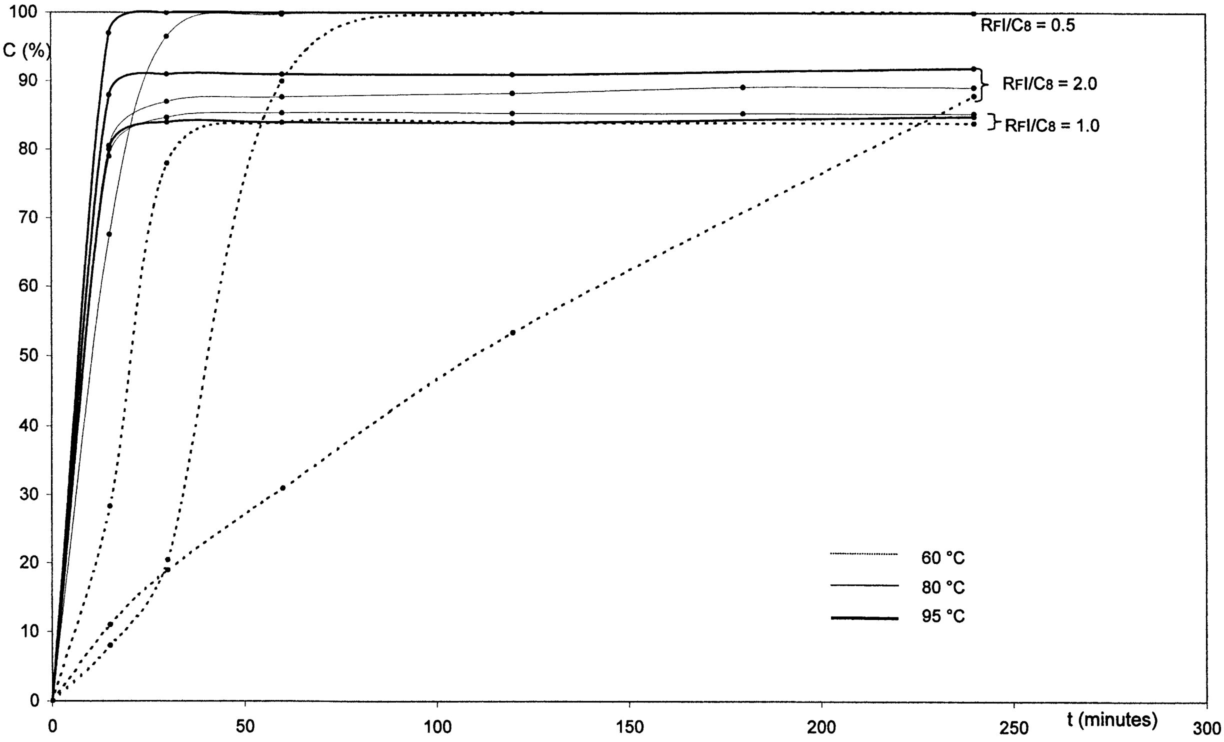

Fig. 1. Conversion vs. time for the addition of perfluorooctyl iodide to 1-octene under the different conditions adopted (AIBN/LR = 0.15).

95°C, respectively, employing equimolar amounts of reactants or a molar excess (2:1) of one of them.

The time profiles for conversion under the different reactions conditions adopted are illustrated in Fig. 1. The AIBN amount is presented as the molar ratio to the LR and maintains a constant value (0.15 moles/mole). As can be seen, an excess of 1-octene ($R_FI/C_8 = 0.5$) always leads to an almost complete conversion of the perfluorinated reactant. The use of an excess of perfluoroalkyl iodide ($R_FI/C_8 = 2.0$) leads instead to conversions only slightly higher than those obtained using equimolar amounts of reactants. Increasing the temperature has the expected effect of accelerating the reaction. This effect is not marked when reactants are in an equimolar ratio, while it is pronounced when an excess of one of them is used. With an excess of the fluorinated reactant reaction was very slow at 60°C (even though the final value of conversion is nearly as high as those obtained at the higher temperatures). When the optimal conditions are employed (95°C, excess of olefin) complete conversion can be attained in less than 20 min.

A particular event was also observed at the beginning of the reaction. In the initial phase the temperature of the reaction mixture rises to a value which is significantly higher than the bath temperature. Fig. 2 illustrates the profiles obtained for the temperature of the reaction mixture for experiments conducted using an excess of the fluorinated reactant. As can be seen, in the initial phase the bulk temperature reaches values near 150°C (when using a bath temperature of 95°C) and 130°C (when using a bath temperature of 80°C). However, at 60°C a much less significant thermic peak is observed much later. The profiles resulting for the reaction conducted with reactants in an equimolar ratio are illustrated in Fig. 3; in this case the internal temperature reached even higher values (156 and 152°C at bath temperatures of 95 and 80°C, respectively). When an excess of olefin was used the highest values measured for the internal temperature were considerably lower (120°C as maximum value at bath temperature of 80°C) even though under these conditions the highest conversion was obtained.

2.2. Gel phase formation

The aforementioned procedure followed by the reductive dehalogenation of the iodinated intermediate was used to obtain samples with different weight percentages of $F(CF_2)_8(CH_2)_8H$. These samples were then combined to prepare three other samples 60, 70 and 80% pure (GLC values) which were used as starting materials in the treatments with the solvents.

The bath temperature used to form the gel phase was in this case lower than that previously used for $F(CF_2)_8(CH_2)_{18}H$ (−15°C as compared to 20°C, [1]). In fact, due to its shorter hydrogenated segment, the solubility in alcohols of $F(CF_2)_8(CH_2)_8H$ is higher, so under conditions of high DRs and/or low initial sample purity (IP) it was necessary to cool the mixture to a lower temperature in order to obtain the gel phase.

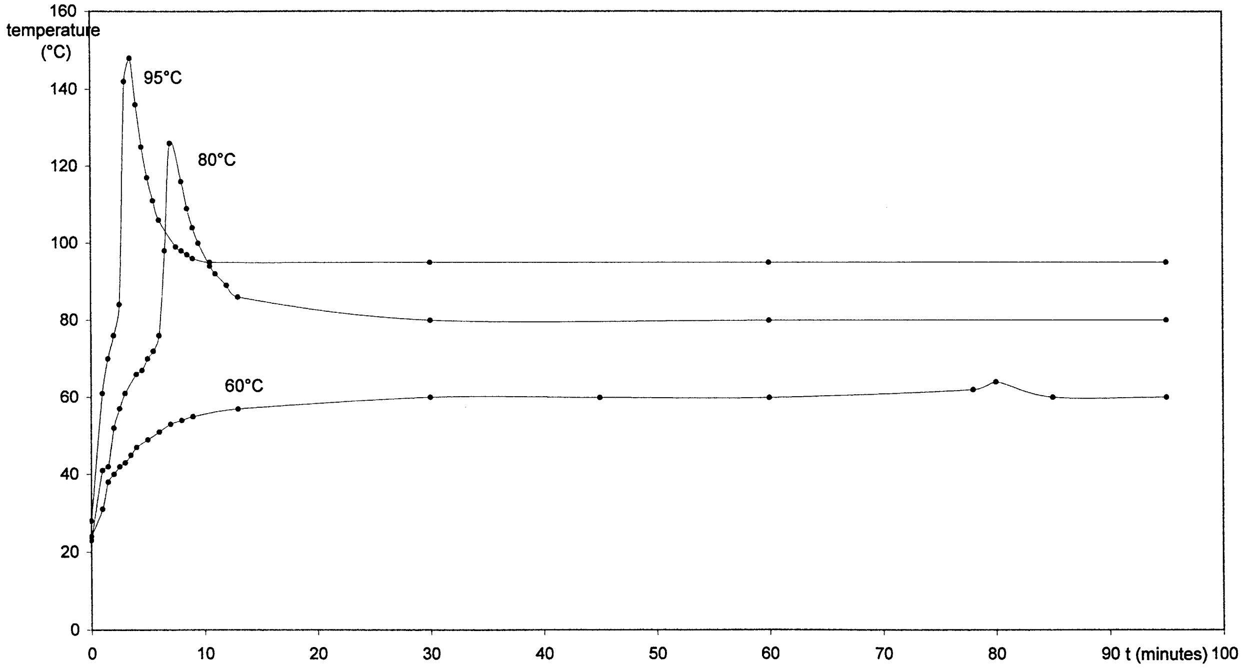

Fig. 2. Thermic peaks observed at the beginning of the addition of perfluorooctyl iodide to 1-octene when an excess of fluorinated reactant was used ($R_FI/C_8 = 2.0$; $AIBN/C_8 = 0.15$).

2.2.1. Cooling rate

Under strictly controlled conditions the cooling rate (CR), defined as the time required for the solution to reach the bath temperature, should be the same for all the experiments. But this parameter, which can have some influence on the gel phase structure [14], strongly depends on the process variables influencing the gel phase formation (i.e. DR and initial purity of the sample), as expected due to its effect on the amount of the gel phase formed. In Fig. 4 the CR is plotted against DR for the different IPs. CR (°C/min) was calculated

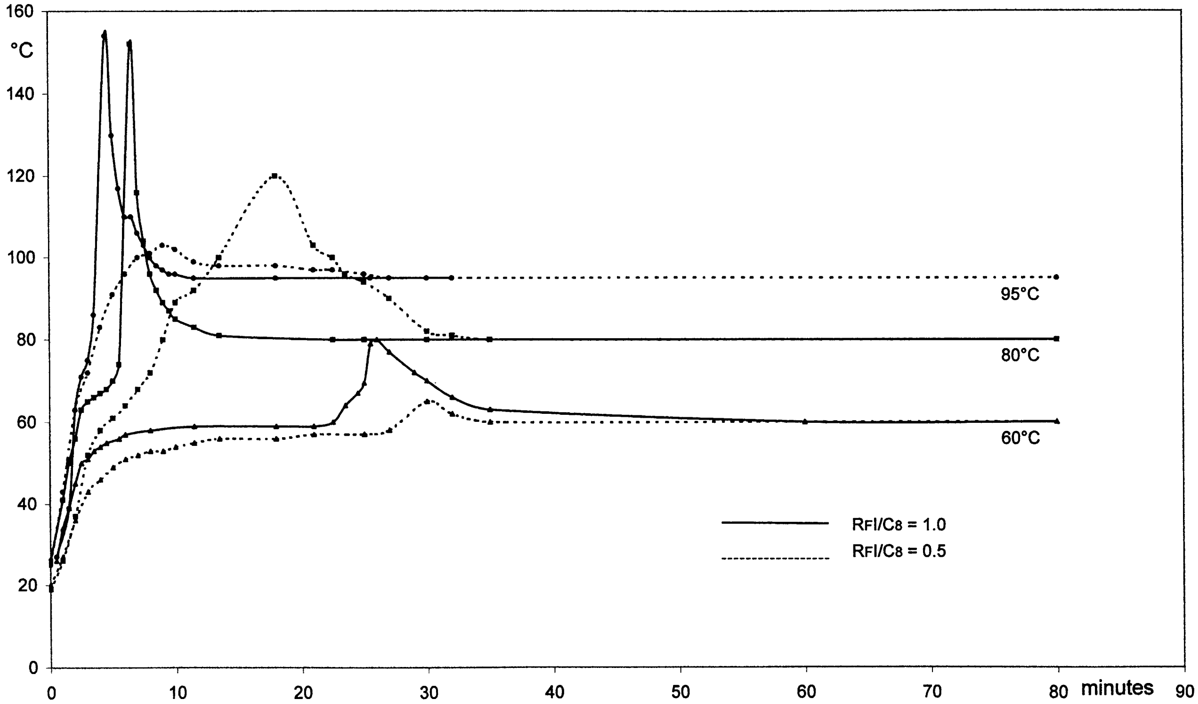

Fig. 3. Thermic peaks observed at the beginning of the addition of perfluorooctyl iodide to 1-octene when reactants in an equimolar ratio or an excess of the olefin were used ($AIBN/R_FI = 0.15$).

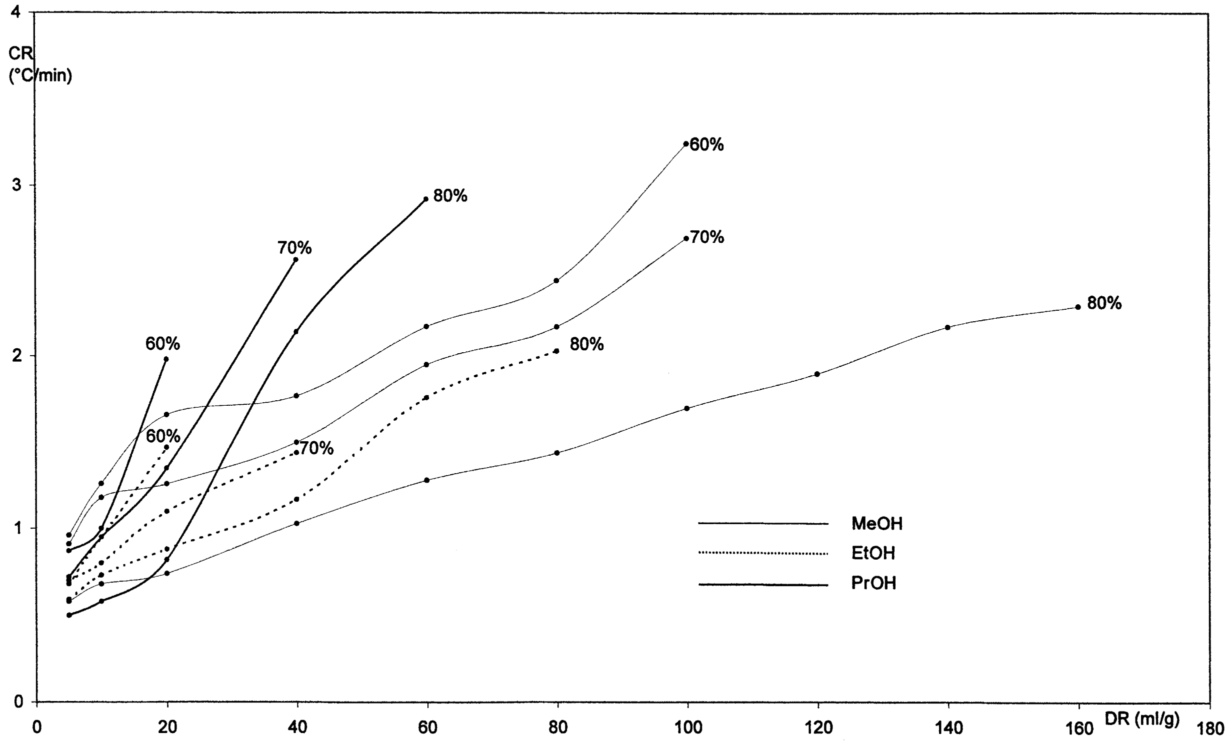

Fig. 4. CR vs. DR for the gel phase formation from samples of $F(CF_2)_8(CH_2)_8H$ with different initial purity in the solvents used.

from the equation:

$$CR = \frac{\Delta T}{t} \tag{1}$$

where ΔT (°C) is the difference between the initial and final temperatures of the experiment, and t (min) the time required for the solution to reach the bath temperature. For each solvent the CR increases as the IP decreases and as the DR increases showing the influence of these two parameters on t, since in this case ΔT is almost constant. Therefore, t depends on the amount of the gel phase formed, i.e. it is short under conditions giving little gel phase (high DR, low purity) and vice versa. Indications on the relative solubilizing power of the solvents used can also be drawn from Fig. 4. Methanol is the worst solvent because it forms gel phase also at high DRs (up to 160 ml/g). Propanol is the best solvent for samples about 80% pure, whilst for lower purities it is comparable with ethanol.

The observed variations on the CR were not however considered important for the purpose of the current work, given that in previous experiments on $F(CF_2)_8(CH_2)_{18}H$ [8] significant variations of this parameter did not show appreciable influence on the results obtained. Therefore, this parameter has not been taken into particular account in this study.

2.2.2. *Gel point*

The temperature at which the gel phase begins to form (*gel point* (GP)) is another significant parameter which depends on the process variables employed. The GP can be determined from curves of °C versus *time* because, due to the crystallization heat on cooling, the bulk temperature remains more or less constant for some time. Determination of the GP was generally easy for $F(CF_2)_8(CH_2)_{18}H$ [8]. Instead for $F(CF_2)_8(CH_2)_8H$, due to its higher solubility in alcohols, the GP was sometimes difficult to accurately measure in spite of the lower bath temperature, especially when a high DR was employed and/or the purity of the treated sample was low. Fig. 5 illustrates an example of the change in the bulk temperature with time for experiments conducted in ethanol on samples 80% pure using different DRs; in this case the GP values can be easily determined.

The variations in GP values with respect to changes in the process variables are illustrated as a example in Fig. 6 for experiments carried out in ethanol under different DRs and IPs. GP increases with increase in IP and decrease in DR. Analogous behavior was observed for the other two solvents, even if comparison between them highlights a certain influence of the DR on the relative GP. As can be seen in Fig. 7, under conditions of high concentration (low DR, 10 ml/g) the determined GP is more or less the same for all solvents, whilst the relative values become more and more different as the DR increases. This may be explained by considering that under conditions of high concentration, the differences in the solubilizing power of solvents are nearly insignificant while they tend to become more and more important as the dilution increases.

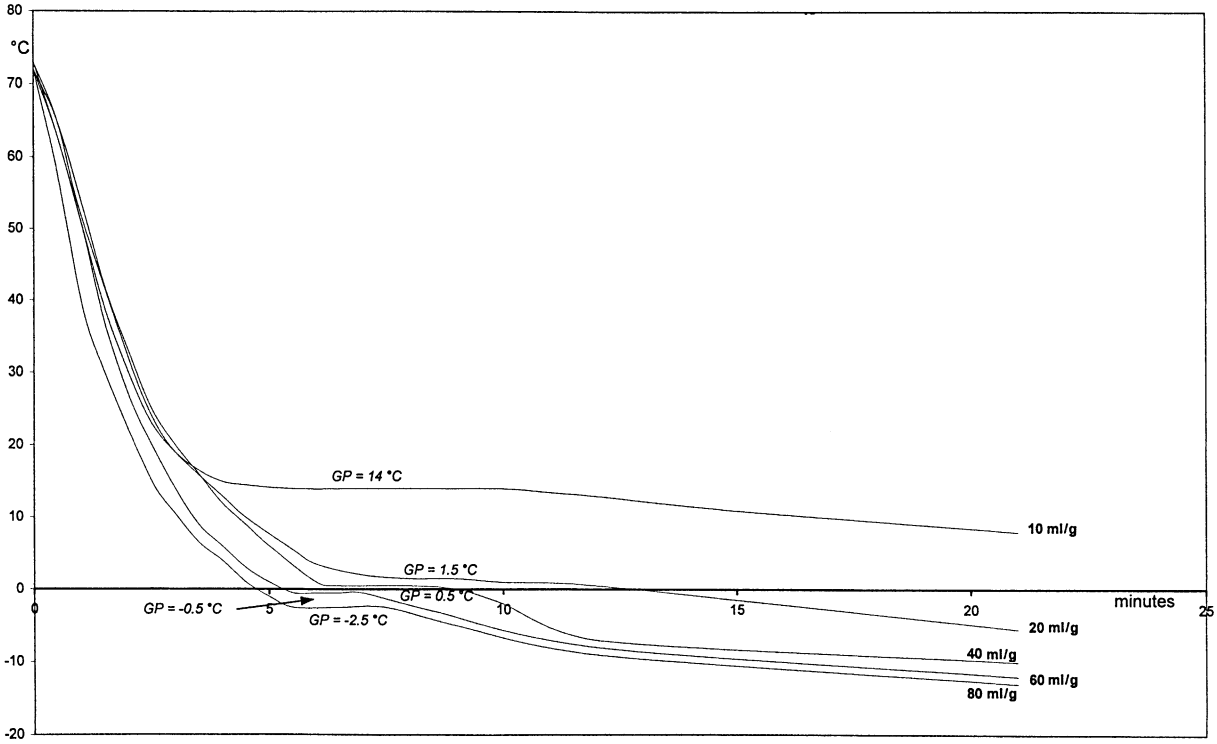

Fig. 5. GP values determined at different DRs during gel phase formation from samples of 80% pure $F(CF_2)_8(CH_2)_8H$ in ethanol.

2.2.3. Evaluation of the gel phase formation process

The treatment of semifluorinated alkanes with solvents leading to a gel phase can be considered as a type of crystallization process and used as a purification method for these compounds. For an evaluation of the effectiveness of this treatment it is important to take into account both the quantitative side (i.e. the recovered amount of sample with respect to the treated amount (wt.%)) and the qualitative one

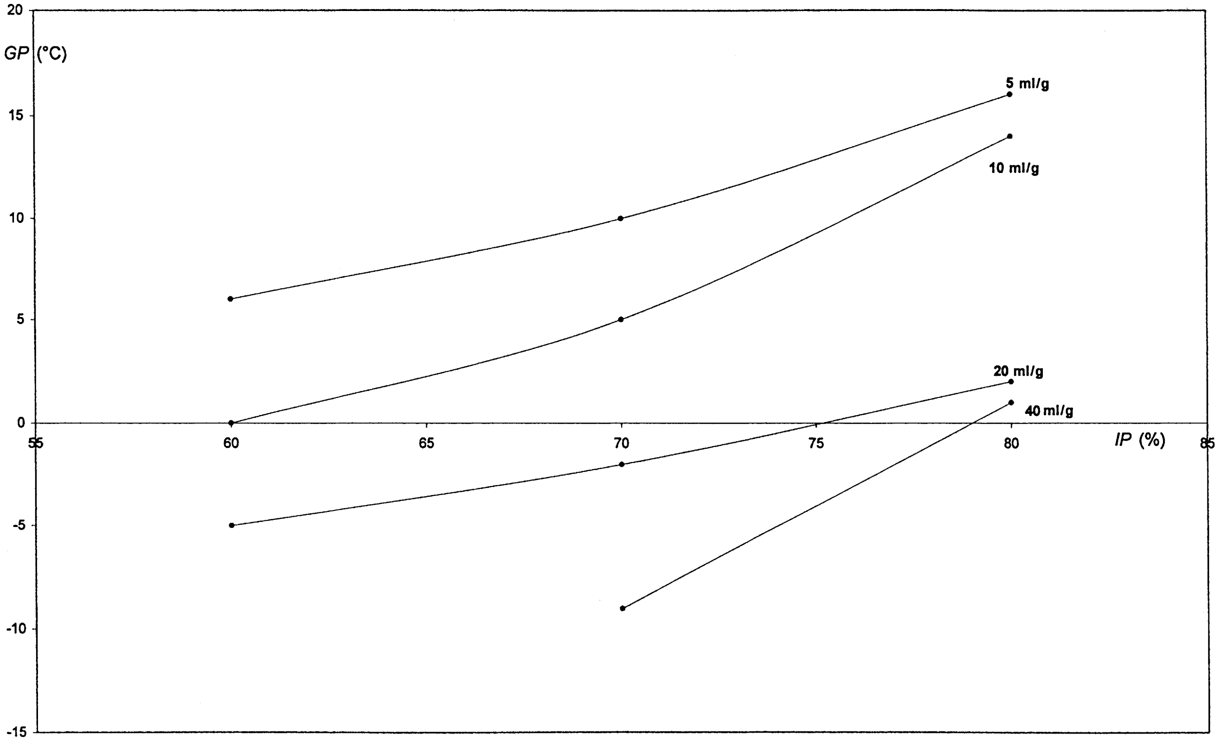

Fig. 6. Dependence on the IP of the GP at different DRs using ethanol as solvent.

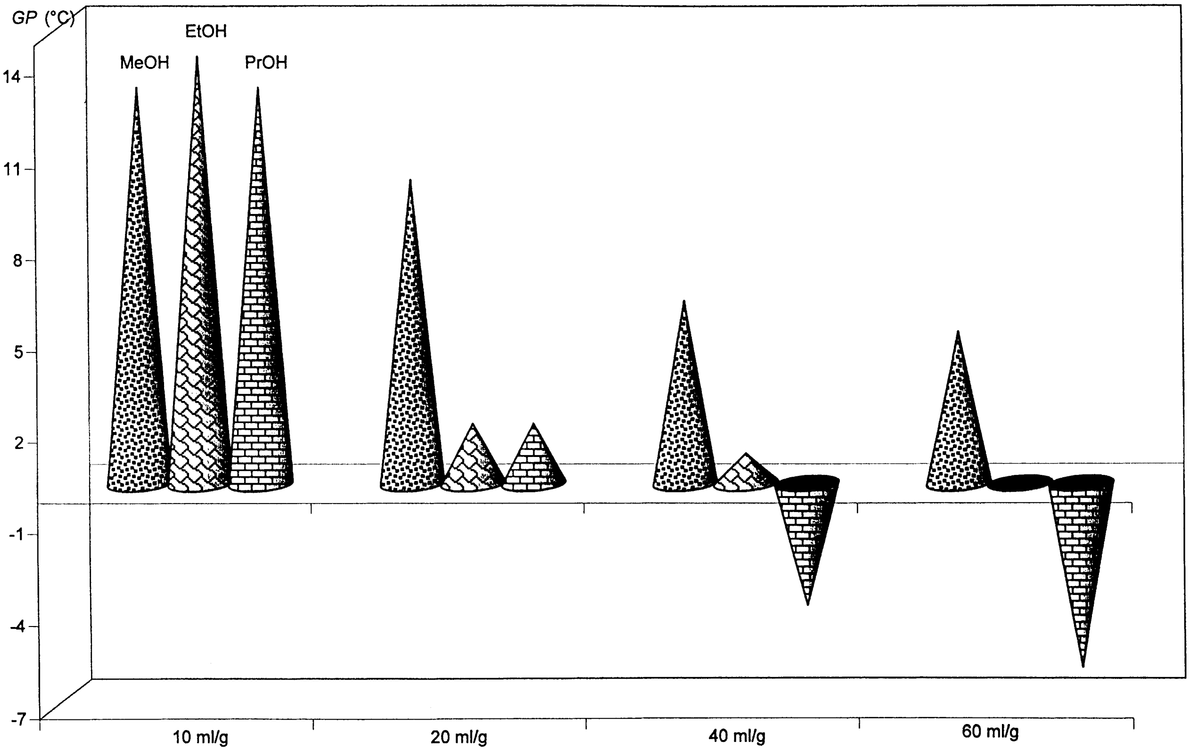

Fig. 7. Influence of the DR on the GP in the different solvents used.

(i.e. the improvement in the sample purity (imp%)). In particular, the sample purity improvement was calculated as follows:

$$\text{imp\%} = 100\left[\frac{(\text{FP} - \text{IP})}{\text{IP}}\right], \tag{2}$$

where FP and IP are respectively the final and initial percentages of $F(CF_2)_8(CH_2)_8H$ determined in the treated sample. These aspects were at first taken into account separately in the experiments; then they were unified in a single parameter (%*Y*) to give an overall evaluation of the process, as follows:

$$\%Y\,(\text{yield}) = \frac{[(\text{wt.\%}) \times (\text{imp\%})]}{100} \tag{3}$$

The change in wt.% on alteration of the process variables (IP and DR) is reported as an example in Fig. 8 for the experiments carried out using ethanol as solvent. All curves show a maximum corresponding to a DR of 10 ml/g and a decreasing profile for higher values of this parameter. This effect can be explained by considering that for DRs less than 10 ml/g (i.e. 5 ml/g) the solution is oversaturated, so the amount of sample dissolved is limited by the low available volume of solvent and thus the amount of sample recovered from the gel phase, with respect to that treated, will be low. On increasing the DR to 10 ml/g the amount of sample dissolved increases due to the greater available volume of solvent and the amount of sample recovered from the gel phase will be higher. When the DR is further increased solution becomes more and more dilute and thus results in a smaller amount of sample being recovered from the gel phase.

The behavior observed in propanol was very similar, except that the gel phase was not obtained for DRs higher than 60 ml/g, because of the before mentioned greater solubilizing power of this solvent. For experiments conducted with methanol curves wt.% versus ml/g followed a very different course, as can be seen in Fig. 9 where the profiles obtained for 70% pure samples in the three alcohols are compared. The curve obtained when methanol was used as the solvent exhibits a very different profile from the other curves. This is due to the lower solubilizing power of this solvent which permits gel phase formation at high DRs.

In Fig. 10 the dependence on the process variables for the improvement of the sample purity (imp%) are reported for experiments conducted in propanol. The different profiles observed for samples with different initial purities could be explained considering that the improvement of the sample purity principally depends on the following factors:

1. the recrystallization of part of the solute to form the gel phase;
2. the amount of impurities coming from the solution retained inside the gel phase and remaining in the sample after the solvent removal.

Both factors are similarly influenced by the amount of the gel phase formed since an increase in the gel formed leads to

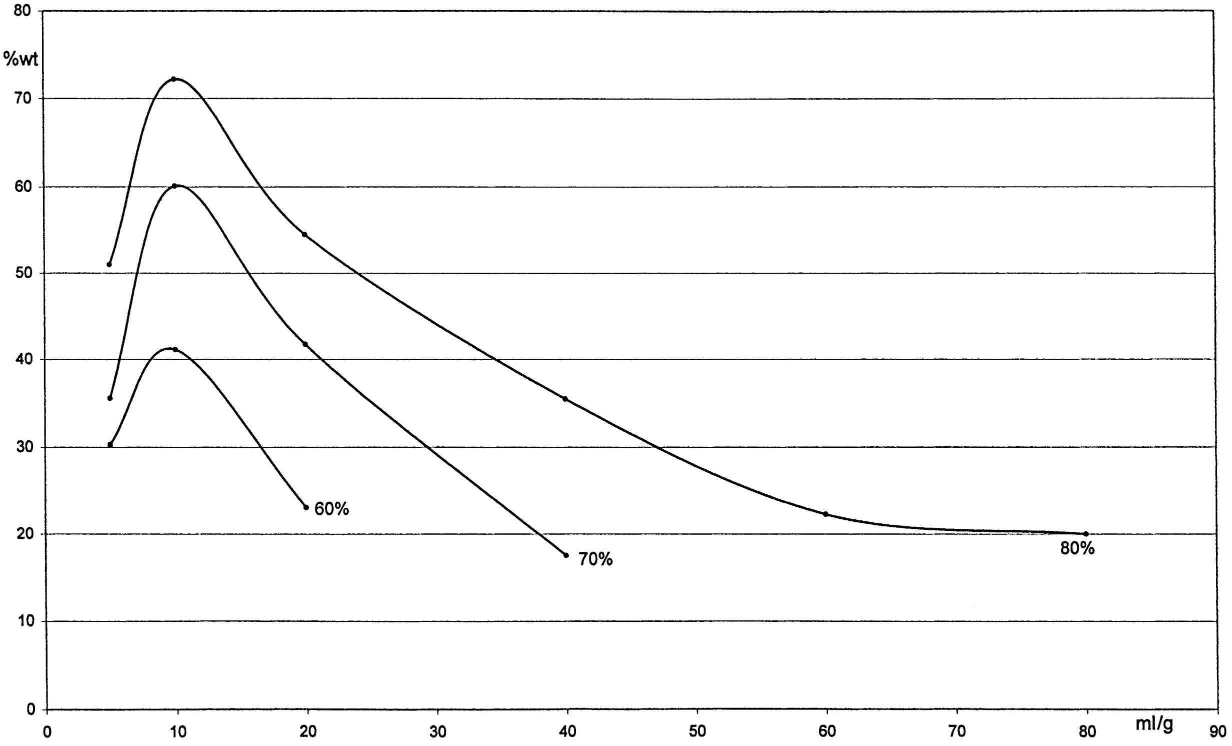

Fig. 8. Influence of DR and IP on the recovered amount of the treated sample (ethanol as solvent).

a small quality improvement. In the case of Fig. 10, for dilutions below 10 ml/g the system can be considered to be under supersaturation conditions due to the small volume of solvent. Thus, when the DR increases from 5 to 10 ml/g the greater available volume of solvent increases the amount of solute; consequently a larger amount of gel phase is obtained (see Fig. 8) thus leading to a lower improvement in the purity of the treated sample. Further addition of solvent leads the

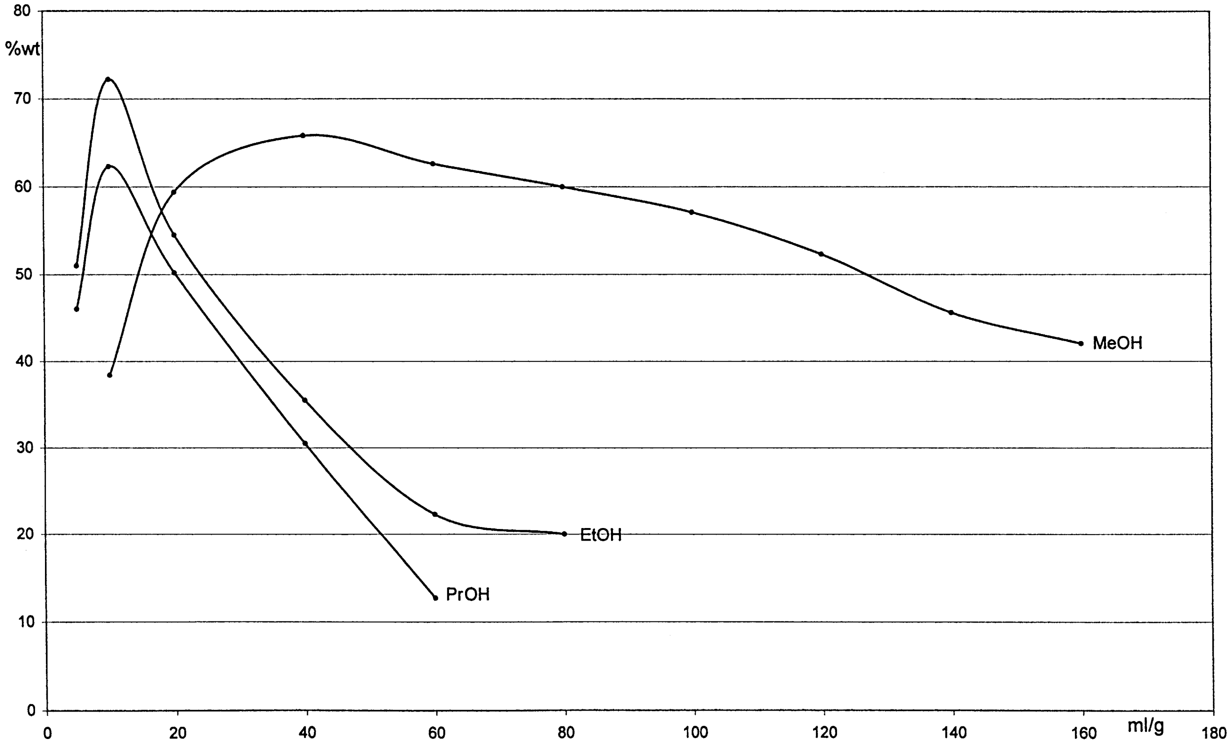

Fig. 9. Different profiles of the curves wt.% vs. ml/g observed for 70% pure samples in the three alcohols used.

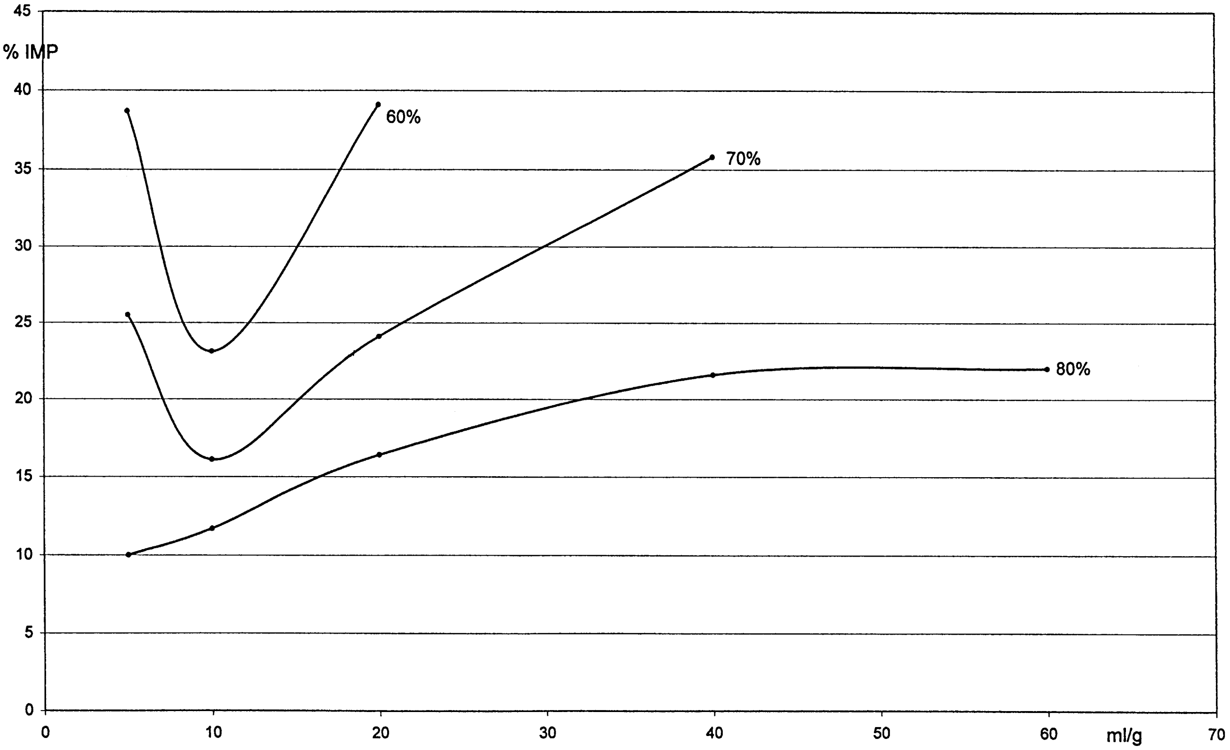

Fig. 10. Dependence on DR and IP for the purity improvement of the treated sample (propanol as solvent).

system beyond the solubility limit and the quality of the gel phase will increase either due to the lower quantity of gel phase formed or to the lower concentration of impurities in the solution. These effects are more important for samples having a low initial purity (60 or 70%) because they contain a significant amount of impurities; in fact, the corresponding curves show a minimum at 10 ml/g. Samples with a higher initial purity (80%) do not show a minimum because factor (b) becomes less important.

Analogous behavior was observed for the experiments carried out using ethanol as the solvent, while methanol led to a quite different behavior that will be discussed later.

By arrangement of these two parameters (wt.% and imp%) according to Eq. (3) it was possible to determine the change of the parameter $\%Y$ with the process variables to give a overall evaluation of the effectiveness of the treatment. In Fig. 11 the values of $\%Y$ calculated from Eq. (3) for the experiments carried out with ethanol and propanol on samples having different initial purities are plotted versus the DR. All profiles present a maximum ($\%Y_{\mathrm{max}}$) that individualizes the DR giving the highest treatment yield for each value of the IP. For each solvent this maximum shifts towards higher DRs as the IP increases.

The experiments conducted in methanol exhibit quite different behavior, as detailed in Fig. 12 where both imp% and $\%Y$ are plotted versus the DR for different initial purities of the treated samples. A certain similarity can be noted in the profiles of these two parameters with respect to dilution which suggests that in this case $\%Y$ is more influenced by imp% than by wt.%. In particular, curves $\%Y$ versus ml/g do not present a significant maximum thus making it impossible to identify the DR giving the highest treatment yield.

A plot of $\%Y_{\mathrm{max}}$ values versus the degree of purity of the treated samples permits comparison of the solvents used with respect to the relative yields obtained for the treatment (Fig. 13). Due to its lower solubilizing power, methanol gives the highest yield for samples having a purity lower than about 75%; propanol or ethanol are more suitable for samples of higher purity, even though this effect is not very pronounced. However, $\%Y_{\mathrm{max}}$ always decreases as the purity of the treated sample increases.

Finally, in Fig. 14 the DRs giving the $\%Y_{\mathrm{max}}$ values ($(\mathrm{ml/g})_{\mathrm{max}}$) are plotted against the initial purity of the treated samples. From these results it is possible to determine the DR giving the highest treatment yield for each solvent and any sample purity. For methanol, 20 ml/g is the most effective DR in every case. For ethanol and propanol the best DR increases with the sample purity to about 80%, where the differences between the solvents vanish and 20 ml/g is the most effective DR for all of them.

2.2.4. Comparison with $F(CF_2)_8(CH_2)_{18}H$

On the basis of the parameter $(\mathrm{ml/g})_{\mathrm{max}}$ a comparison can be made between $F(CF_2)_8(CH_2)_8H$ and the homologous $F(CF_2)_8(CH_2)_{18}H$, on which an analogous study was carried out previously [8]. In Fig. 15 the changes in $(\mathrm{ml/g})_{\mathrm{max}}$ relative to the IP for both the semifluorinated compounds in methanol and ethanol are compared (the values for $F(CF_2)_8(CH_2)_{18}H$ are drawn from [8]). The solvents react very differently to the structures of the treated compounds.

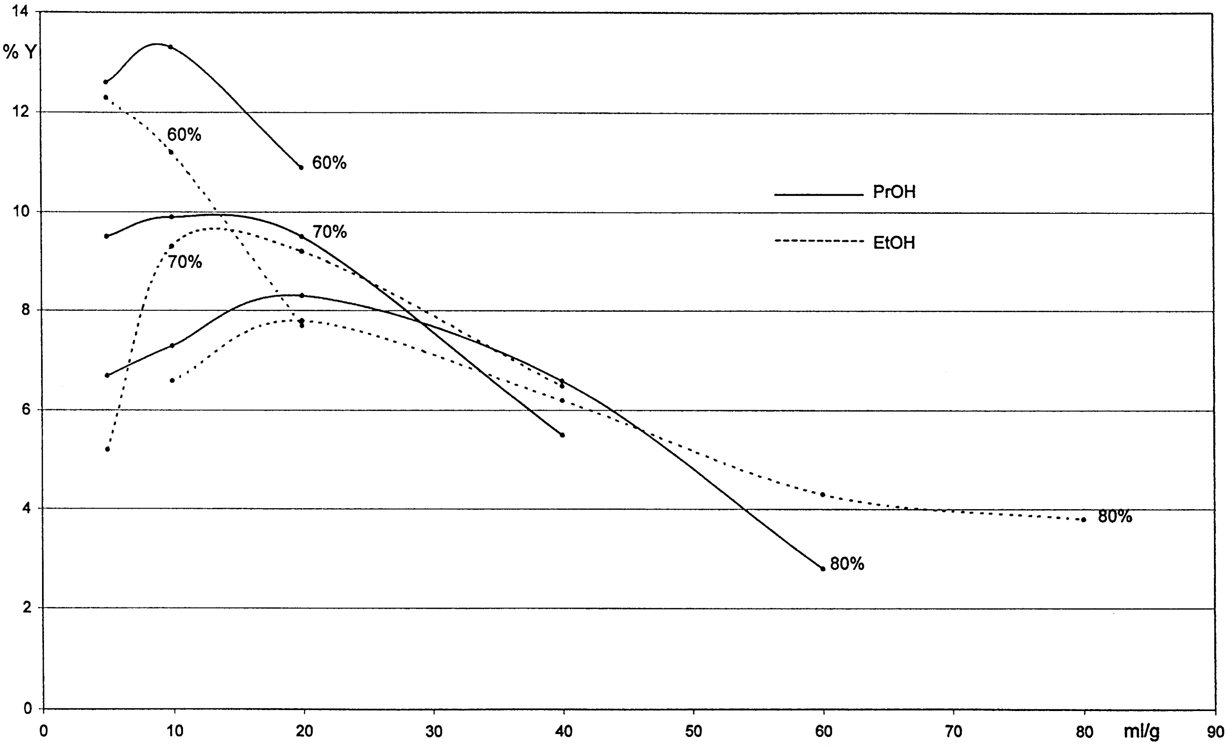

Fig. 11. Profile of %Y vs. ml/g determined in ethanol and propanol for samples with different initial purity.

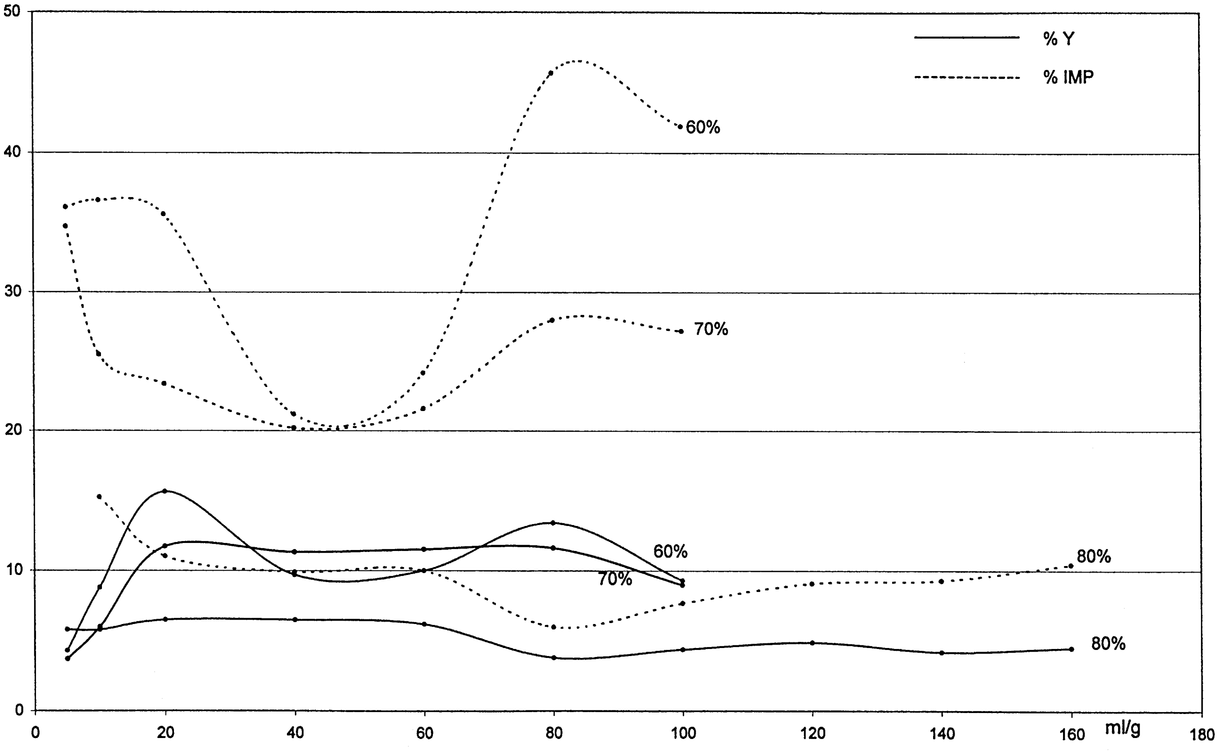

Fig. 12. Influence of the DR on %Y and imp% for treatments in methanol of samples with different initial purity.

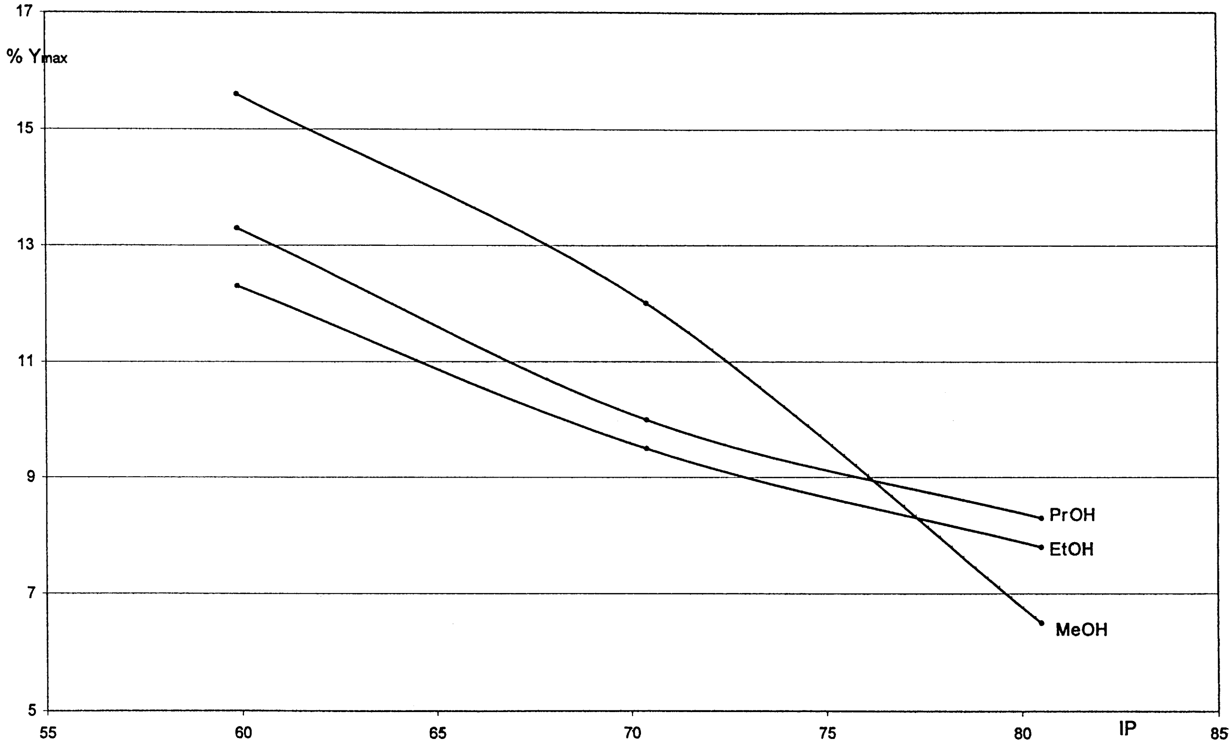

Fig. 13. Maximum effectiveness (%Y_{max}) vs. the IP determined for the three alcohols used as solvent.

In fact, while in ethanol $(ml/g)_{max}$ slightly increases changing from $F(CF_2)_8(CH_2)_8H$ to $F(CF_2)_8(CH_2)_{18}H$, for methanol this increase is much more marked. This is a consequence of the lower solubilizing power of this solvent towards these semifluorinated compounds, strongly influenced by the length of their hydrogenated fragments.

Another difference in the behavior of these two compounds is shown in Table 1, where the values determined for

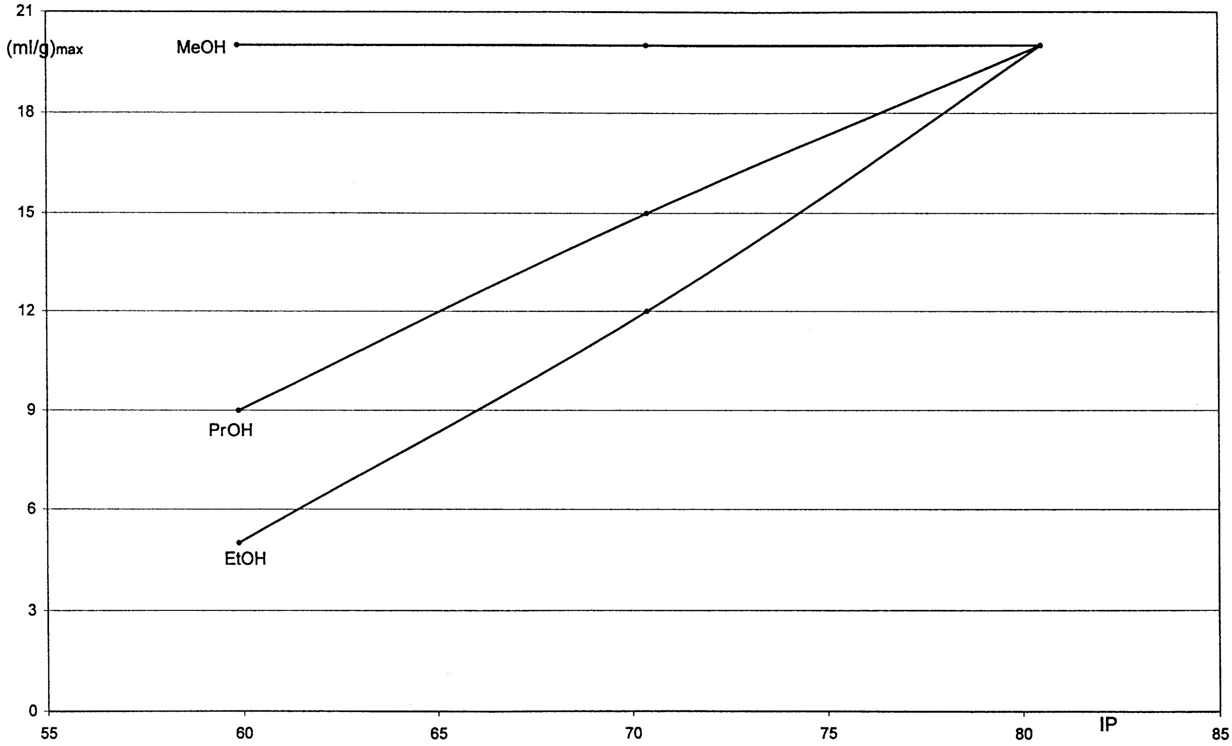

Fig. 14. DR giving the maximum effectiveness ($(ml/g)_{max}$) vs. the IP determined for the three solvents used.

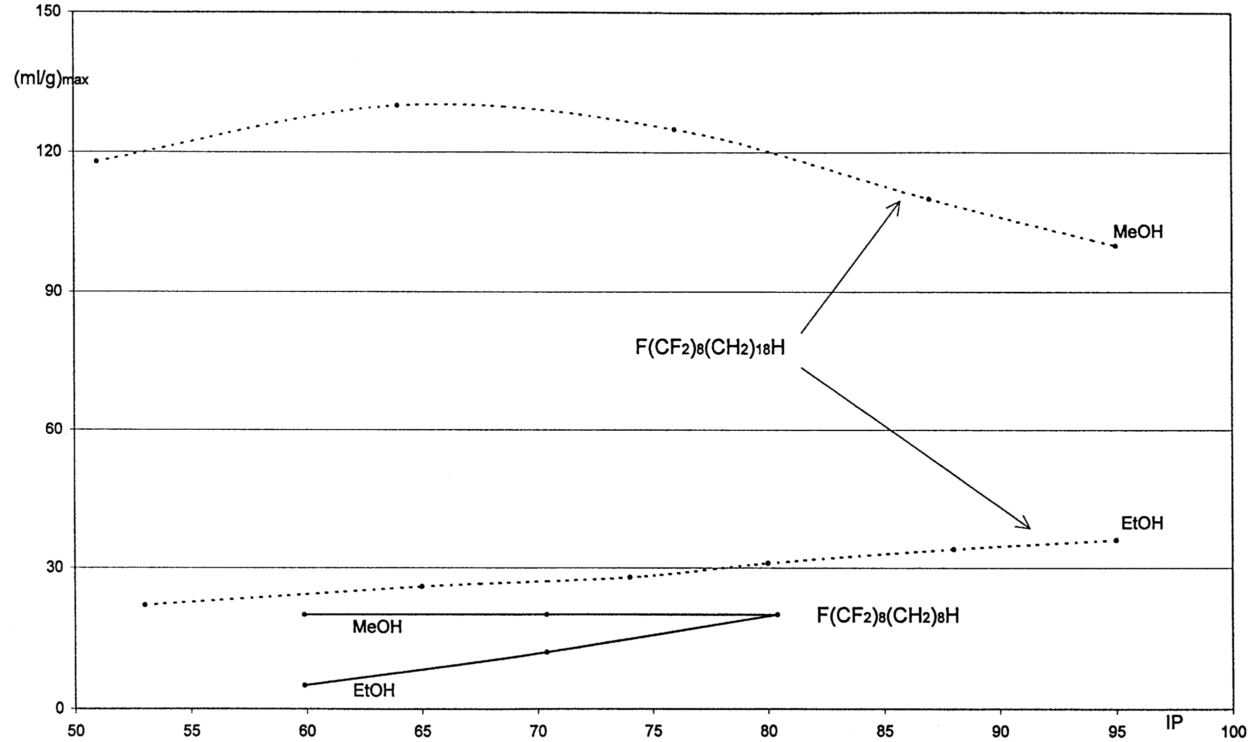

Fig. 15. Comparison between the profiles of $(ml/g)_{max}$ vs. the IP determined in methanol and ethanol for $F(CF_2)_8(CH_2)_8H$ and $F(CF_2)_8(CH_2)_{18}H$.

Table 1
Comparison between the $\%Y_{max}$ values determined for $F(CF_2)_8(CH_2)_8H$ and $F(CF_2)_8(CH_2)_{18}H$ in methanol and ethanol

	Compound								
	$F(CF_2)_8(CH_2)_8H$			$F(CF_2)_8(CH_2)_{18}H$[a]					
	60[b]	70[b]	80[b]	65[b]	74[b]	80[b]	64[b]	76[b]	87[b]
Methanol	15.6	12.0	6.5	–	–	–	47	17	8
Ethanol	12.3	9.5	7.8	28	21	15	–	–	–

[a] Values from reference [8].
[b] Initial purity (%).

$\%Y_{max}$ using methanol and ethanol as solvent at different IPs are compared. As can be seen, for $F(CF_2)_8(CH_2)_{18}H$ the values are significantly higher than those determined for $F(CF_2)_8(CH_2)_8H$, especially with ethanol and at low IPs.

3. Conclusions

With respect to the first step of the reaction leading to $F(CF_2)_8(CH_2)_8H$ the experimental data demonstrate that an excess of the unsaturated reactant and a temperature of 95°C result in complete conversion of the fluorinated reactant in a very short time. Important exothermic events were also observed at the beginning of this reaction.

The experiments carried out in alcohols with samples of $F(CF_2)_8(CH_2)_8H$ having different degrees of purity made it possible to ascertain the influence that the treatment variables have on the gel phase formation, with particular reference either to the quantitative (percent of sample recovered with respect to the amount treated) or to the qualitative (percent improvement in purity of the sample treated) aspects. On the basis of these two parameters it was possible to define the overall effectiveness of this treatment as a purification method for these fluorinated compounds. The use of three homologous alcohols as solvent allowed the comparison of their behavior and determination for each of them of the DR (ml of solvent per g of sample) leading to the highest treatment yield ($(ml/g)_{max}$).

As the overall treatment yield observed generally tends to decrease as the purity of the treated sample increases (see Fig. 13), this treatment with alcohols could be used as a method for purifying these semifluorinated compounds for samples of low purity. Research is going on to test other classes of solvents which may be suitable for an advanced purification of these compounds by means of their gel phase formation.

4. Experimental

4.1. Materials and procedures

$F(CF_2)_8(CH_2)_8H$ was synthesized according to the usual two-step procedure consisting of a free-radical initiated addition of perfluoroalkyl iodides to 1-olefins followed by reductive dehydroiodination with Zn and hydrogen chloride of the iodinated intermediate so formed [9–11]. A representative experiment is described here.

In a 250 ml three-necked round-bottom Pyrex glass vessel equipped with a thermometer, water-cooled condenser and an outlet drain tube were placed 75.0 g (0.137 moles) of $C_8F_{17}I$ (Hoescht, 97% pure), 7.7 g (0.068 moles) of C_8H_{16} (Aldrich, 90% pure) and 1.7 g (0.010 moles) of AIBN (Jansenn, 98% pure). The vessel was repeatedly purged with nitrogen through the condenser, then heated at 80°C for 4 h. The reaction was followed by GLC analysis of samples periodically drawn from the vessel by the drain tube. A small positive pressure of nitrogen (20 mmHg) was maintained inside the vessel in order to facilitate this periodic withdrawal.

The final reaction mixture (68.8 g) was distilled at reduced pressure in order to recover the unreacted reagents. The residue (44.5 g) was dissolved in ethanol (100 ml) and added dropwise to a vigorously stirred mixture of zinc powder (10 g) in ethanol (100 ml) in a 1 l three-necked Pyrex glass vessel equipped with mechanical stirrer and two two-necked adaptors to accommodate thermometer, water-cooled condenser, and two dropping funnels for the addition of reactants. A 36% aqueous HCl (25 ml) was added simultaneously at such a rate that a vigorous foam was maintained throughout the reaction mixture. After all the zinc had reacted, the crude $F(CF_2)_8(CH_2)_8H$ was recovered, washed with water and dried over anhydrous sodium sulfate.

The gel phase formation was studied by following the procedure described in [8], using ethanol (Prolabo, 99.8% pure), methanol (C. Erba, 99.9% pure) or 1-propanol (Lab-Scan, 99.5% pure) as solvent. In order to minimize the influence of the experimental variables, the treatments were all conducted using vessels having the same volume (400 ml) and shape, dipped into the bath at the same depth, and starting from the same initial temperature (i.e. the boiling point of the solution) for each solvent. The following procedure was always adopted.

A weighed sample of the semifluorinated compound was added to 250 ml of solvent in a 400 ml Pyrex beaker. The resultant mixture was then brought to a gentle boil with vigorous magnetic stirring. In this manner a partial or complete dissolution of the sample was obtained according to the employed DR and the initial purity of the sample. The vessel was then quickly transferred to a bath maintained at −15°C and allowed to cool. The change in the internal temperature was measured using a thermometer placed in the center with the bulb 1 cm from the bottom. It was often possible to determine the corresponding ‘‘gel point’’, i.e. the temperature at which the gel phase begin to form [8]. When the thermometer registered −15°C the gel phase was recovered by filtration under vacuum, removing the liquid phase as far as possible. The gel phase was then oven-dried at 40°C, weighed and analyzed.

4.2. Analysis

GLC analysis of samples was carried out on a Perkin-Elmer Sigma 3 instrument connected to a Sigma 1 G.C. system for quantitative determinations. For the addition reaction of $C_8F_{17}I$ to C_8H_{16} a 2 m × 2 mm stainless steel column packed with OV 101 (10%) was used with the following temperature program: 25°C for 15 min, 5°C/min to 250°C (He as gas carrier at 20 ml/min, flame ionization detector). Analytical data were used to define the extent of conversion of the limiting reagent under different conditions. Conversion was calculated by the following equation:

$$X = \left[\frac{(M_i - M_t)}{M_i}\right] \times 100, \tag{4}$$

where M_i and M_t are respectively the initial moles and those at time t for the limiting reagent. M_i and M_t were calculated for each analyzed sample by GLC internal standard methods [12,13], using perfluorohexyl iodide and heptane as internal standards for perfluorooctyl iodide and 1-octene, respectively.

Samples recovered from the gel phases were dissolved in diethyl ether (1:10 v/v) and the same column was used with the following temperature program: 150°C for 5 min, then 3°C/min to 250°C (He as gas carrier at 20 ml/min, flame ionization detector).

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