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EXPERIMENTAL SURFACE ACTIVITY MEASUREMENTS OF SOME FLUORINATED COMPOUNDS IN A NON-AQUEOUS MEDIUM*

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SUMMARY

Surface activity of some fluorinated compounds having the structure R_F-R_H (R_F- = fully fluorinated group; R_H- = fully hydrogenated group) in vaseline oil was experimentally determined by surface tension measurements at 20 °C. The surface tension *vs* concentration isotherms allow comparison of the behaviour of the tested compounds, particularly with regard to the relationship between surface activity and fluorinated group length of the solute.

INTRODUCTION

The fluorinated organic compounds usually employed as surface agents in non-aqueous media have molecular structures with the organophobic and organophilic constituents generally bounded to polar functional group (amide or carboxylic ester) [2,3,4]. Some particular fluorinated compounds have a typical unbranched molecular structure R_FR_H, where a fully fluorinated part R_F- (organophobic) is directly linked to a fully hydrogenated part R_H- (organophilic). The

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absence of polar functional groups could make these compounds particularly interesting with respect to their performance as surface agents in non-aqueous media. Therefore several of these compounds having structures liable to give useful information about their surface activity were synthesized [1]. In analogy with previous experiments [4], vaseline oil was used as the non-aqueous medium.

EXPERIMENTAL

Materials

Molecular formulae of the compounds tested as surface agents are reported in Table 1. Each compound is identified by a two-number code: the first figure is the number of carbon atoms of the R_F- group, the second one is the number of carbon atoms of the R_H- group.

The R_F-R_H compounds were synthesized by a slightly modified Brace's procedure [6,7]. 1-**Iodoalkane** and 1-alkene, conveniently chosen in order to prepare the expected structure, undergo addition at 80 °C initiated by azobisisobutyronitrile, and give the corresponding adduct:

$$R_FCF_2I + CH_2{=}CHR_H \longrightarrow R_FCF_2CH_2CHIR_H$$

a subsequent treatment with Zn and aqueous HCl leads to the final product:

$$R_FCF_2CH_2CHIR_H \longrightarrow R_FCF_2CH_2CH_2R_H$$

The compounds obtained in this way were then purified by vacuum distillation or crystallization according to their physical state. GLC purity grades of 97-98% were obtained.

Procedure

The non-aqueous medium used was the Prolabo "Rectapur" vaseline oil (density: 0.86-0.89 g/ml; surface tension: 32.3 dynes/cm). The solutions were prepared by adding a known amount of fluorinated compound to a weighed amount of vaseline oil; then the mixture was warmed slightly under magnetic stirring to ensure complete solution. Before surface tension measurements were made, each solution was allowed to stand for 24 hours in a thermostat at the established temperature.

Surface tensions were determined by the du Noüy method employing a Krüss K8600 interfacial tensiometer (platinum ring circumference: 60 mm, wire diameter: 0.37 mm, accuracy: ± 0.1 dynes/cm). Measurements were carried out at 20 ± 0.2 °C and at 50 ± 0.4 °C.

TABLE 1

Formulas and codes of the tested fluorinated compounds

formula	**code**
$C_4F_9C_8H_{17}$	4.8
$C_4F_9C_{14}H_{29}$	4.14
$C_4F_9C_{16}H_{33}$	4.16
$C_4F_9C_{18}H_{37}$	4.18
$C_6F_{13}C_8H_{17}$	6.8
$C_6F_{13}C_{12}H_{25}$	6.12
$C_6F_{13}C_{16}H_{33}$	6.16
$C_8F_{17}C_8H_{17}$	8.8
$C_8F_{17}C_{12}H_{25}$	8.12
$C_8F_{17}C_{14}H_{29}$	8.14
$C_8F_{13}C_{16}H_{33}$	8.16
$C_8F_{17}C_{18}H_{37}$	8.18

TABLE 2

Solubility limits for some of the tested fluorinated compounds

compound	solubility limit
6.8	$>$ 0.35 mol/l
6.12	$>$ 0.35 mol/l
6.16	0.148 mol/l
8.8	0.085 mol/l
8.12	0.057 mol/l
8.16	0.041 mol/l

Many of the tested compounds showed good solubility at 20 °C to concentrations even higher of 0.3 mol/l. However in some cases, particularly with the compounds prepared from $C_8F_{17}I$, very poor solubilities were observed. Solubility limits at 20 °C for some of the compounds are reported in Table 2; these values were determimed by cloud point measurements. Surface tensions of some pure compounds are given for a comparison in Table 3.

RESULTS AND DISCUSSION

Surface activity of each fluorinated solute in the vaseline oil is given by the surface tension *vs* concentration isotherms reported in the following diagrams. Dotted lines are for measurements carried out with opalescent samples; the corresponding surface tension values are therefore approximate, but they are useful in order to compare the different compounds with respect to their surface activity.

Figure 1 shows the surface tension *vs* concentration isotherms for the fluorinated compounds prepared from C_4F_9I (having therefore the shortest R_F- group). These compounds show good solubility in the vaseline oil at least to concentrations of 0.3-0.35 mol/l. As expected, surface tension decreases as concentration increases; furthermore a surface tension depression can be observed as the organophilic portion of the molecule (R_H- group) becomes smaller. This behaviour evidently demonstrates that the surface activity of the solute molecules depends on the F/H ratio (fluorine atoms number/hydrogen atoms number per molecule): the greater the F/H ratio of a given series of compounds having the same R_F- group, the greater the surface tension depression.

This relationship between surface tension depression and organophilic portion of the solute molecule appears clear also from Fig. 2, where the initial slope of each curve of Fig. 1 is plotted *vs* the F/H ratio (these values are reported in Table 4 together with the corresponding values determined for the other compounds). An almost linear decrease for initial slopes can be observed as the R_H- group becomes larger.

TABLE 3

Surface tension of some pure fluorinated compounds

compound	dynes/cm
4.8	20.6*
4.14	22.4*
4.18	20.9°
8.8	18.9°
8.14	20.6°

(*) measured at 20 °C

(°) measured at 50 °C

TABLE 4

F/H ratios and initial slopes $[-(\delta\gamma/\delta c)_i]$ for the tested compounds

compound	F/H	$-(\delta\gamma/\delta c)_i$
4.8	0.53	75
4.14	0.31	50
4.16	0.27	40
4.18	0.24	34
6.8	0.76	170
6.12	0.52	120
6.16	0.39	180
8.8	1.00	260
8.12	0.68	200
8.14	0.59	270
8.16	0.51	290
8.18	0.46	860

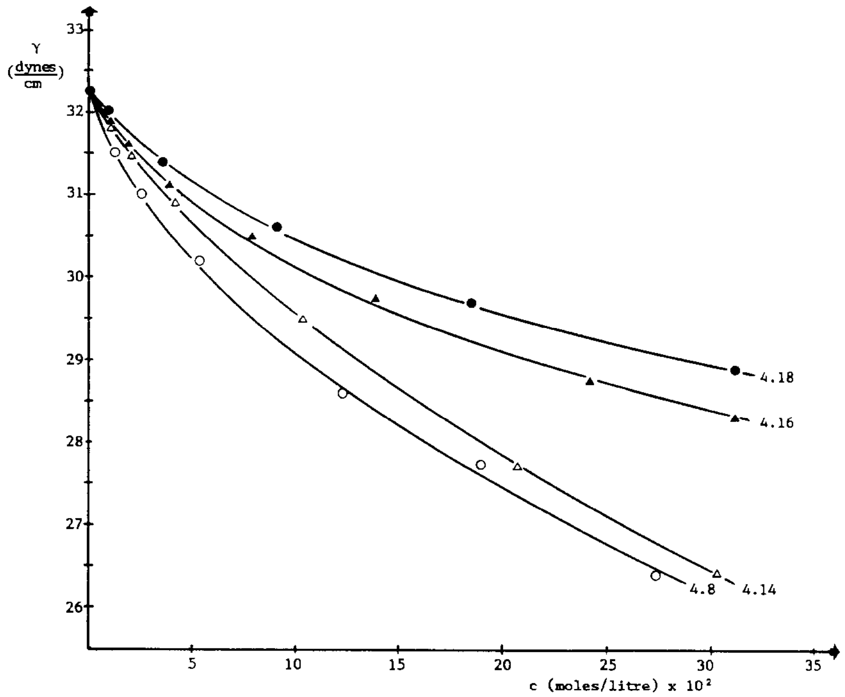

Fig. 1. Surface tension/concentration isotherms for compounds prepared f

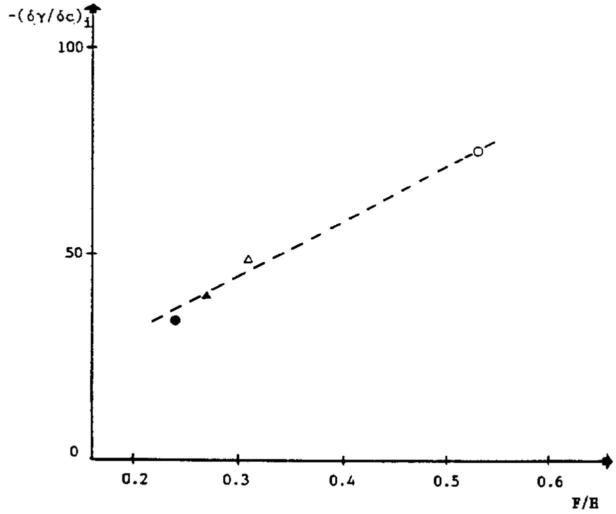

Fig. 2. Initial slopes against F/H ratio for compounds prepared from C_4F_9I (○ 4.8, △ 4.14, ▲ 4.16, ● 4.18).

In Figs. 3, 4 and 5 the surface tension vs concentration isotherms are reported varying the organophobic portion (R_F- group) length for the compounds prepared from C_8H_{16} (Figure 3), $C_{12}H_{24}$ (Figure 4) and $C_{16}H_{32}$ (Figure 5) respectively. Also for these compounds a surface tension depression can be observed, which increases as the size of the organophobic group increases: the compounds with the longest fluorinated group C_8F_{17}- show the greatest surface activity within each series, even if their solubility in the vaseline oil is very low. This confirms that surface activity depends on the fluorinated portion of the solute molecule and increases with its length. That results also from data reported in Fig. 6, where the initial slope of each isotherm for these compounds is plotted *vs* the F/H ratio: it can be seen how within each series with the same R_H- group the surface activity increases as the R_F- chain becomes longer. Besides, the increasing slope of these straight lines as the R_H- group becomes longer demonstrates that the effect of the R_F- chain on the surface tension depression is greater in the compounds with the longest R_H- group.

The relationship between surface activity and length of R_H- chain, previously shown in Fig. 1 for compounds having the shortest fluorinated group C_4F_9-, is no longer held by compounds having the longest R_F- chain. The surface tension vs concentration isotherms reported in Fig. 7 (open points) show in fact a *decrease* of the surface tension depression as the R_H- group becomes shorter. In particular, 8.18 shows the highest surface activity measured. These compounds have furthermore a very low solubility in the vaseline oil, so that 8.18 shows opalescence even at concentrations lower than 0.01 mol/l. In order to verify the behaviour of these compounds under conditions of suitable solubility, the surface tension vs concentration isotherms were determined also at a higher temperature (50 °C). The measured surface tension values are reported in the same Fig. 7 (solid points) and show a change in order between 8.14 and 8.16: in fact, a larger R_H- chain leads to a less marked surface tension depression. This change in behaviour ***might*** be related to the simultaneous viscosity change. In other words, the different behaviour observed at 20 °C for 4.X and 8.X series ***might*** be due to the very high viscosity of the solutions prepared with these last compounds. Measurements of viscosity are in course of carrying out in order to confirm this supposition.

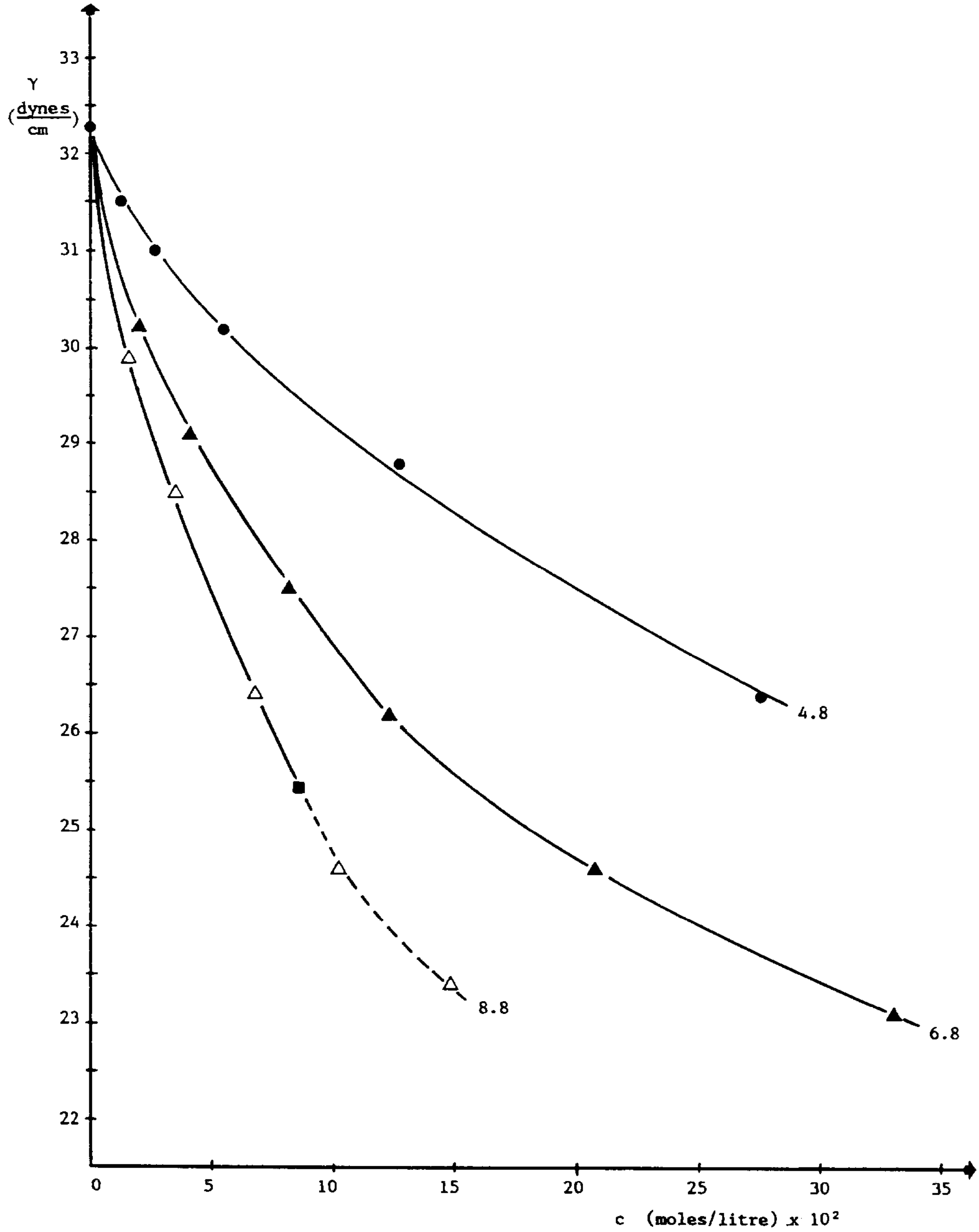

Fig. 3. Surface tension/concentration isotherms for compounds prepared from C_8H_{16} (■ solubility limit).

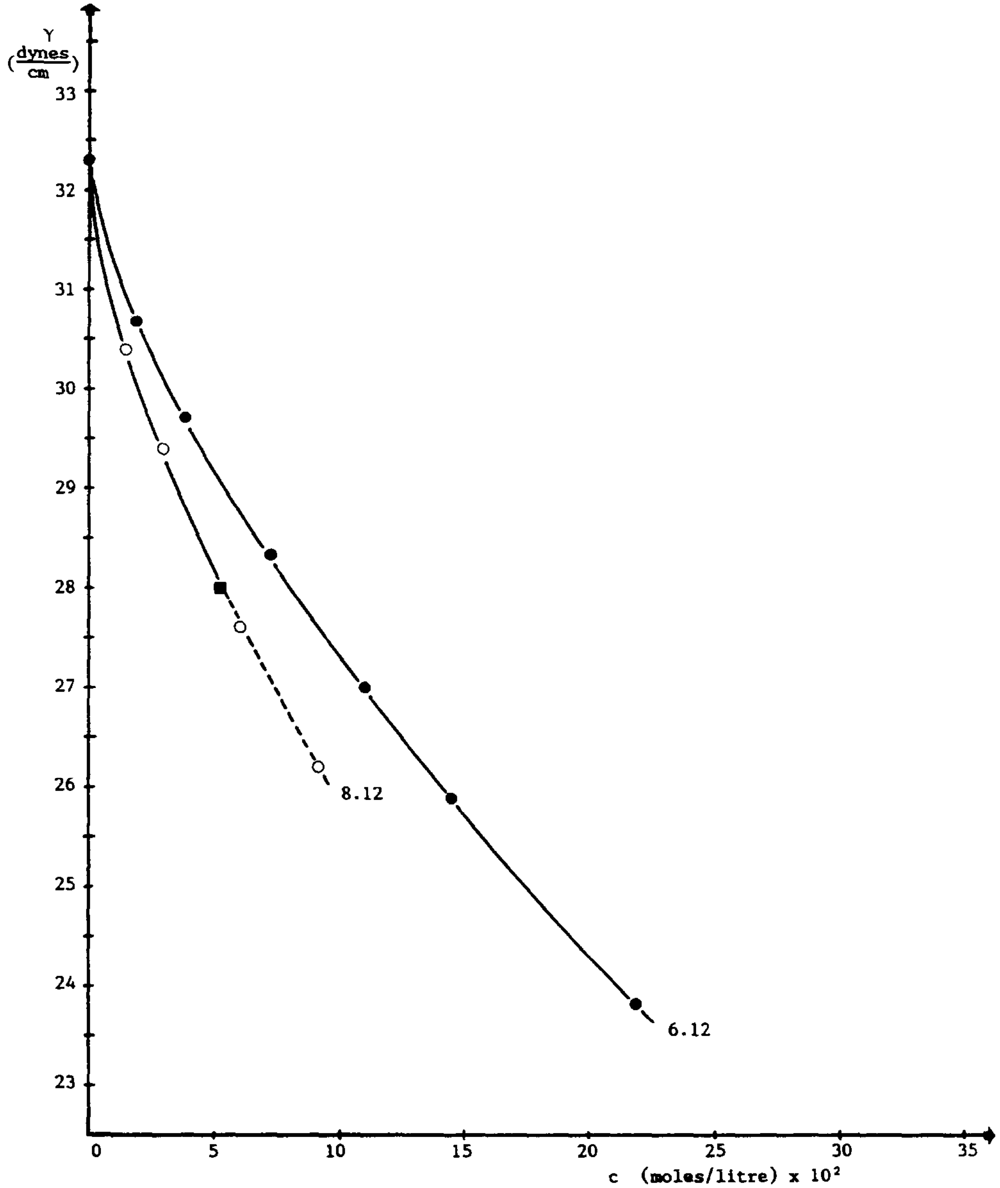

Fig. 4. Surface tension/concentration isotherms for compounds prepared from $C_{12}H_{24}$ (■ solubility limit).

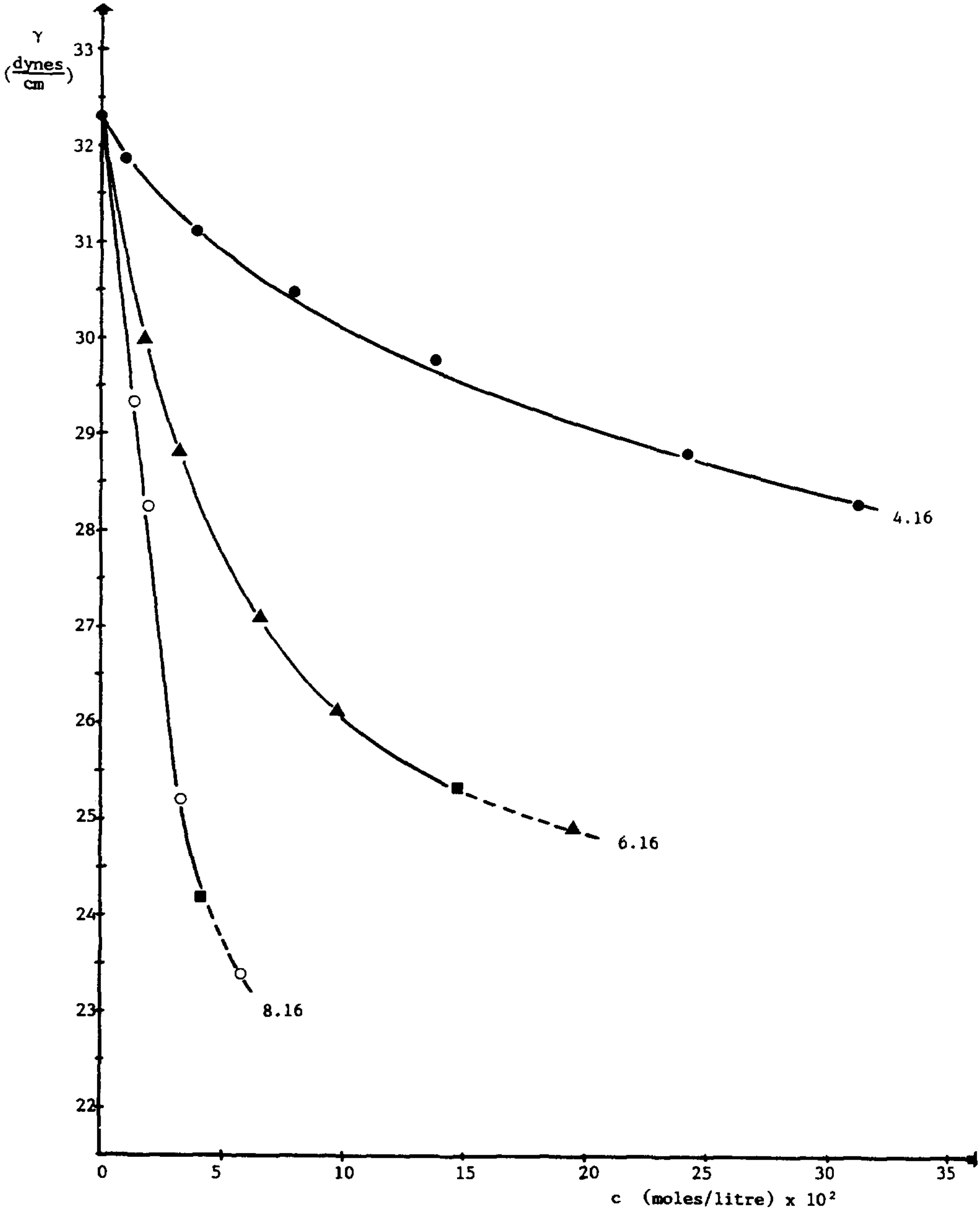

Fig. 5. Surface tension/concentration isotherms for compounds prepared from $C_{16}H_{32}$ (■ solubility limit).

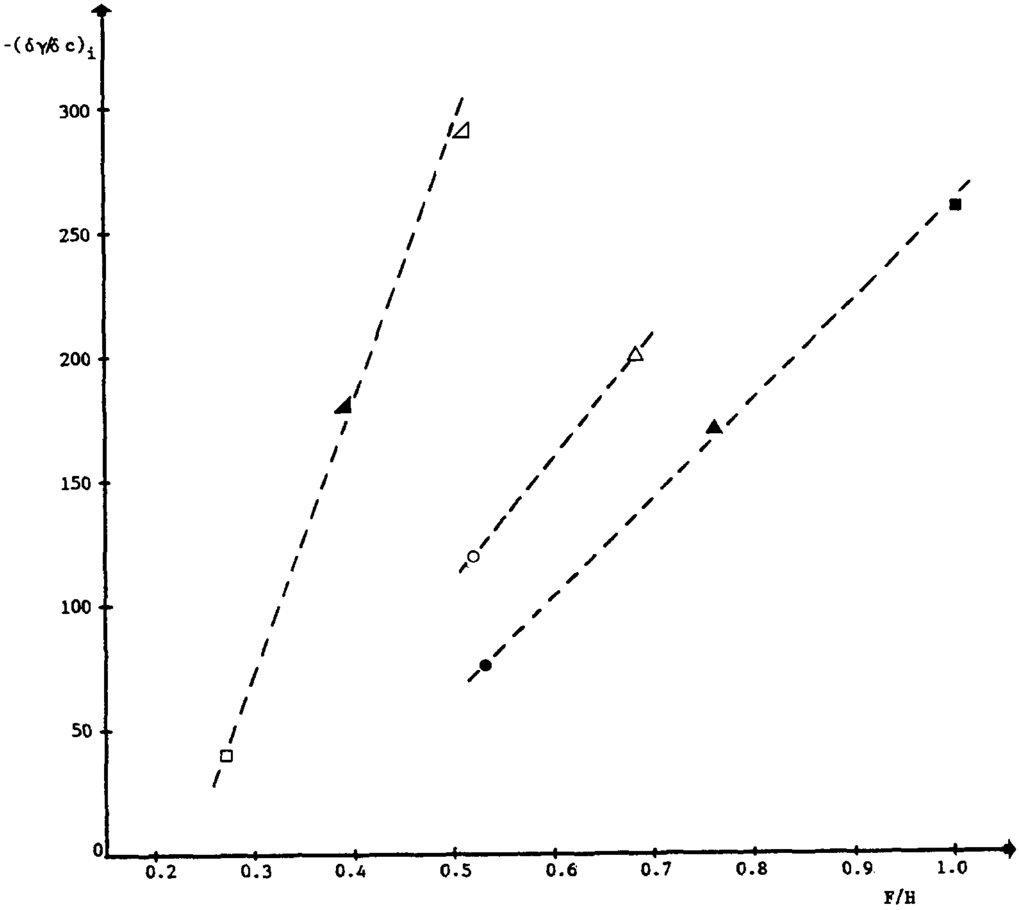

Fig. 6. Correlation between the surface activity (isotherm initial slopes) and the fluorinated group length in some series of the tested compounds (● 4.8, ▲6.8, ■ 8.8, ○ 6.12, △ 8.12, □ 4.16, ◢ 6.16, ◺ 8.16).

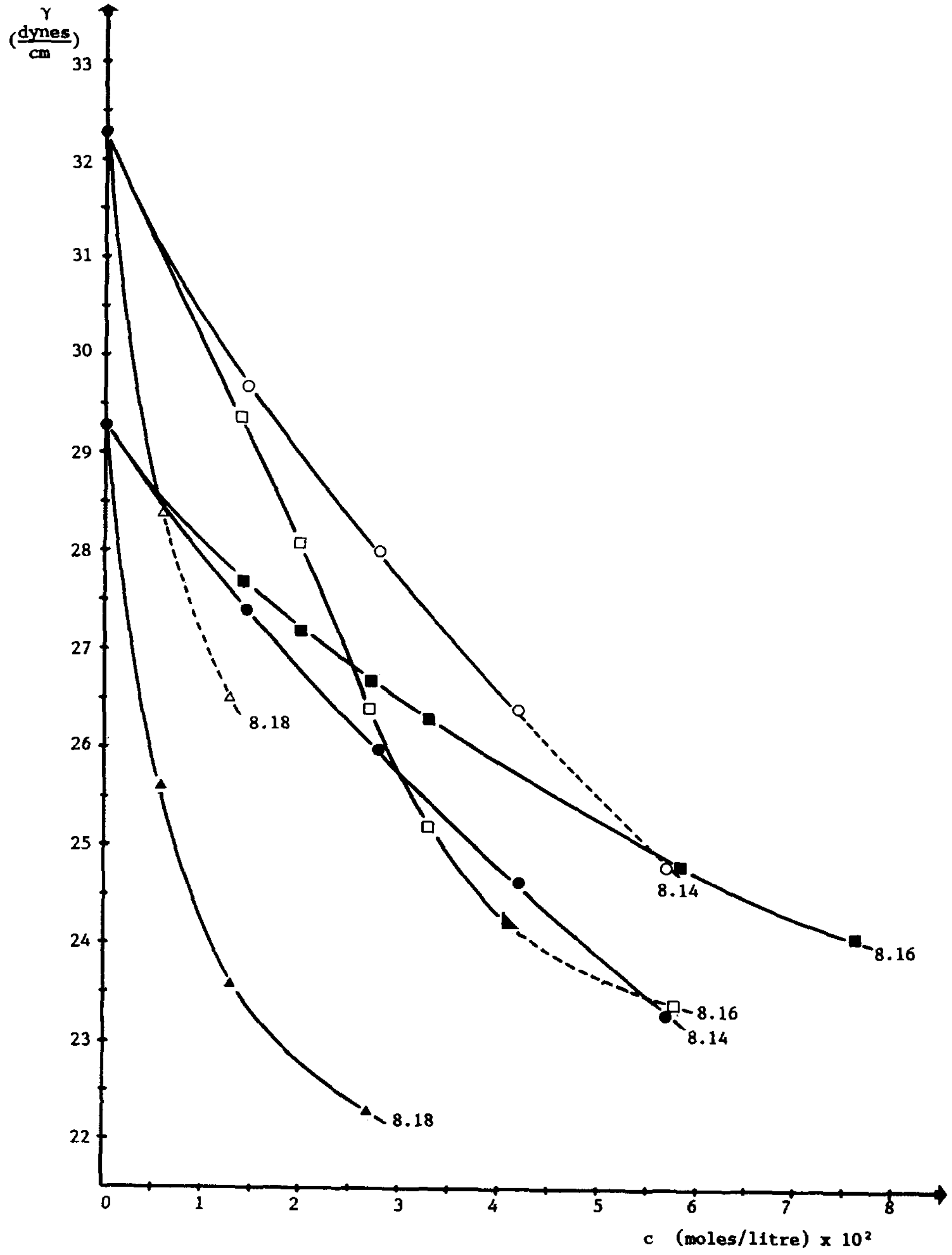

Fig. 7. Surface tension/concentration isotherms at 20 °C (open points) and 50 °C (solid points) for compounds prepared from $C_8F_{17}I$ (◣ solubility limit).

CONCLUSIONS

The reported experimental data show the influence of the organophobic group R_F- on the surface activity of the tested compounds. Almost all these compounds show an increasing surface activity as their fluorinated group becomes larger. Only compounds having the C_8F_{17}- group behave in a different manner; their different behaviour *might* be due to the very high viscosity of their solution in the vaseline oil. In effect, when the viscosity is lowered by a temperature increase, the observed relationship between surface activity and length of the fluorinated chain of the solute molecule is re-established.

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