

NMR Molecular Characterization of Lubricating Base Oils: Correlation with Their Performance

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Abstract. The NMR technique was used to characterize some base oils of different nature (mineral, saturated polyolefins, hydrocracked and from waxes hydroisomerization) at the molecular level. Base oils are used in the formulation of lubricants with the addition of suitable additives which improve the final products performance. The studied base oils are used particularly in the formulation of engine oils. In this paper we have compared two “NMR editing” techniques which allow one to quantify the CH_n ($n = 0\text{--}3$) fractions of an “average” base oil molecule: 1) the gated spin echo (GASPE) and 2) the distortionless enhancement by polarization transfer (DEPT). We found that the quantitative data obtained from GASPE have a better accuracy than those from DEPT and so we chose GASPE to study the molecular characteristics of the aliphatic moieties of the base oils. On the basis of the GASPE data and of the average molecular mass obtained via VPO (Vapor Pressure Osmometry), the average number of branches and aliphatic rings were calculated. Moreover, on the basis of GASPE the distribution of side chain lengths and the positions of the methyl groups along the straight chain (methyls are the only groups for which the positions are directly obtained from NMR spectra) were obtained. A confirmation of the reliability of the NMR approach was achieved by comparing the branching degree, found with the NMR approach, of some base oils with their heats of fusion measured with the Differential Scanning Calorimetry (DSC). The heats of fusion are expected to be directly related to the length of straight CH_2 sequence and therefore to be lower for more branched molecules. We found that for base oils with similar aliphatic moieties, the heats of fusion are lower for more branched base oil molecules with a nearly linear correlation. The exception to this rule is represented by the two olefinic oils. Besides, we found that the fraction of the methyls on aliphatic chains longer than three carbons, determined with GASPE, correlates very well with the pour points values, with the only exception of the mineral oil.

1. Introduction

Base oils used in the formulation of lubricant products are a complex mixture of paraffinic (prevalently branched), aromatic and naphthenic (cycloparaffinic) molecules ranging in carbon number from 20 to 40+. Although most automo-

tive crankcase oils, accessory fluids, and many industrial lubricants contain in excess of 80% base oil in their "finished" formulation, the fundamental molecular relationship between base oil molecular characteristics and product performance remains poorly defined in some applications.

In the last years the demand for improved fuel economy is placing increasing pressure upon engine manufacturers worldwide. So lubricants that can provide additional fuel efficiency benefits are being vigorously sought. A better knowledge of the molecular characteristics and product performance relationship could give a valid tool to find out the desired base oil for "fuel economy" lubricants.

A large number of correlations based on the relative distribution of paraffinic, aromatic and naphthenic type hydrocarbons are reported in literature [1–7] but these studies do not involve the nature and distribution of the aliphatic moieties which, vice versa, determine the low-temperature and rheological properties of base-stocks. ^1H and ^{13}C -NMR techniques have been used to estimate structural parameters in petroleum cuts [8–10] but they have the limitations in resolving the resonance of CH_n ($n = 0\text{--}3$) groups in the aliphatic region.

To overcome the problem of the signal overlap some selected multiplet subspectra ^{13}C -NMR analyses were developed and, in particular, the gated spin echo (GASPE) and distortionless enhancement by polarization transfer (DEPT) have been applied to obtain quantitative CH_n subspectra in petroleum fractions [11–15]. In the present paper we report about the comparison of these two techniques. GASPE resulted to be more reliable than DEPT and was used to characterize six base oils: one mineral, one hydrocracked, two wax hydroisomerized, one polyalphaolefin (PAO) and one polyinternal olefin (PIO). From GASPE spectra the fractional abundances of CH_n , the number and length of branches, the position of methyl groups along the straight chain and the average number of aliphatic rings were obtained.

These molecular characteristics have been correlated with their heats of fusion and they show a nearly linear correlation for not olefinic base oils confirming the reliability of the NMR method to give insight into the branching nature.

2. Experimental Section

The classes and the general properties of the six commercial base-oils are reported in the Table 1.

The detailed hydrocarbon analysis is obtained by a two-step procedure. The first step separates the aromatic and saturate fractions by column chromatography (ASTM D 2549). The saturate subclasses of paraffins and cycloparaffins are measured by a mass spectrometry method (ASTM D 2786). Table 2 contains data for the six different base fluids.

Table 1. List of base oils used in the present work.

Base oil	Type	Kinetic viscosity at 100°C (cSt)	Pour point (°C)	Viscosity, index (VI)
A	Mineral	5.15	-9	105
B	Hydrocracked	4.02	-27	127
C	Wax Hydroisomerized	5.04	-21	146
D	Wax Hydroisomerized	5.73	-24	141
E	PAO	5.82	-60	130
F	PIO	5.70	-40	126

Squalane (Fluka Chemika) was employed as base oil model compounds to evaluate the DEPT and GASPE NMR techniques because it consists of 30 C atoms (which is the mean number of carbons of base oils) and has 6 methyl branches. As cyclic model structure *n*-butyl-cyclohexane (JANSSEN CHIMICA) was used.

Liquid state ^{13}C -NMR were carried out on a Bruker AC 200 (GASPE) and a Varian VXR-400 (DEPT) spectrometer operating at ^{13}C resonance frequencies of 50.288 and 100.555 MHz respectively. Typically, samples were of 20–30 wt% concentration in CDCl_3 . DEPT experiments were carried out using the pulse sequence of Doddrel *et al.* [15] The 90° proton decoupler pulse was accurately measured on 10% ethylbenzene solution in CDCl_3 and its value was estimated to be 25 ps. The 45, 90 and 135° DEPT experiments were collected with $J_{\text{CH}} = 125$ Hz and recycle delays of 8 s. GASPE experiments were carried out using the pulse sequence of Cookson *et al.* [11] by using $J = 125$ Hz and recycle delays of 8 s.

Heats of fusion were measured by differential scanning calorimetry (DSC) using a thermal analyzer (METTLER TA 3000). Approximately 10 milligrams of sample initially was cooled to -130°C using a liquid nitrogen sleeve. The temperature then was ramped at $10^\circ\text{C}/\text{min}$ to nearly 50°C while maintaining a $25\text{ cm}^3/\text{min}$ flow of air over the sample. The heat flow from the sample was recorded as a function of temperature. Heat of fusion was determined by calculating the area of the endothermic peak, an integration of the heat flow vs. temperature signal using a general analysis program.

Table 2. Hydrocarbon analysis of base oils.

Hydrocarbon type (wt%)	A	B	C	D	E	F
Isoparaffins	32.3	75.0	91.9	88.6	87.4	77.6
Cycloparaffins	46.6	20.8	6.9	10.7	12.5	21.5
Aromatics	20.1	3.7	0.5	0.5	0.1	0.9
Polars	1.0	0.5	0.4	0.2	0.0	0.0

Molecular weights of base oils were measured with a Knauer Vapour Pressure Osmometer in toluene solution at the temperature of 70°C.

3. Results and Discussion

Squalane was used as base oil model compound to value which editing NMR technique (GASPE or DEPT) is more accurate to obtain the quantitative fractions of CH_n subgroups. The molecule of squalane has the following CH_n groups: $(\text{CH})_6(\text{CH}_2)_{16}(\text{CH}_3)_8$.

The respective CH_n fractions are therefore:

$$F(\text{CH}_n) = (\text{CH}_n / \sum_n \text{CH}_n),$$

$$F(\text{CH}) = 0.20, \quad F(\text{CH}_2) = 0.53, \quad F(\text{CH}_3) = 0.27.$$

In Figs. 1 and 2 the CH_n subspectra obtained with GASPE and DEPT respectively are reported: as is evident, the GASPE spectra show very low cross-contamination (presence of peaks of other subspectra), while cross-contamination is manifest in all DEPT subspectra. The $F(\text{CH}_n)$ fraction calculated from the GASPE and DEPT are the following:

$$\text{GASPE:} \quad F(\text{CH}) = 0.21, \quad F(\text{CH}_2) = 0.53, \quad F(\text{CH}_3) = 0.26,$$

$$\text{DEPT:} \quad F(\text{CH}) = 0.21, \quad F(\text{CH}_2) = 0.56, \quad F(\text{CH}_3) = 0.23.$$

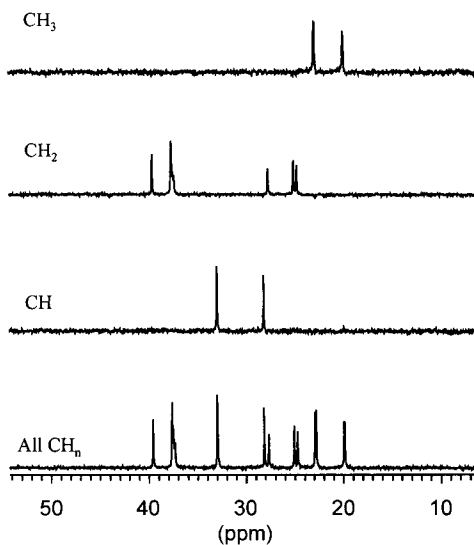


Fig. 1. Conventional ^{13}C -NMR spectrum of squalane (bottom). The GASPE subspectra are labeled according to the component resonance types as “CH”, “ CH_2 ”, and “ CH_3 ”.

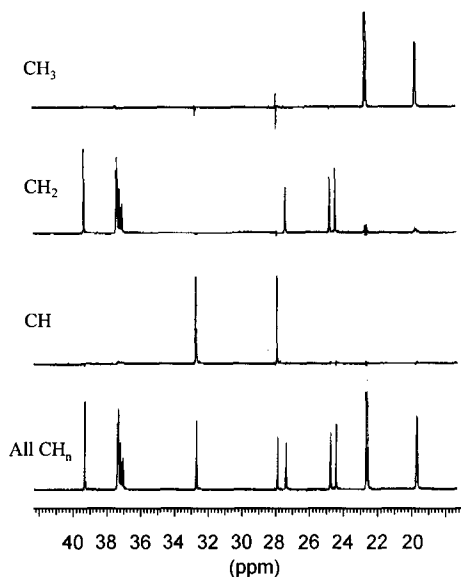


Fig. 2. Conventional ^{13}C -NMR spectrum of squalane (bottom). The DEPT subspectra are labeled according to the component resonance types as “CH”, “ CH_2 ”, and “ CH_3 ”.

From these data (comparing them with those expected) GASPE technique results are more accurate.

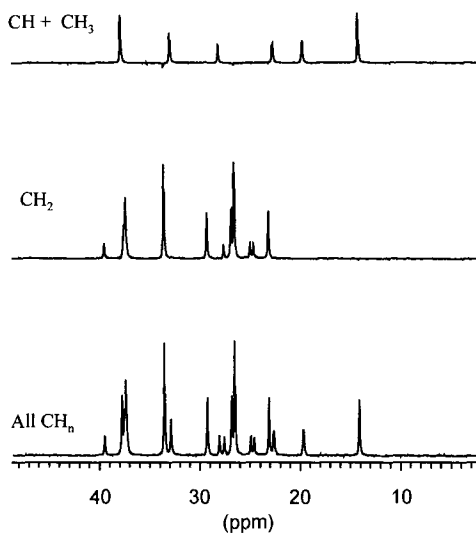


Fig. 3. Conventional ^{13}C -NMR spectrum of a mixture of 33 wt% of squalane and 67 wt% of *n*-butyl-cyclohexane (bottom). The GASPE subspectra are labeled according to the component resonance types as “ CH_2 ” and “CH + CH_3 ”.

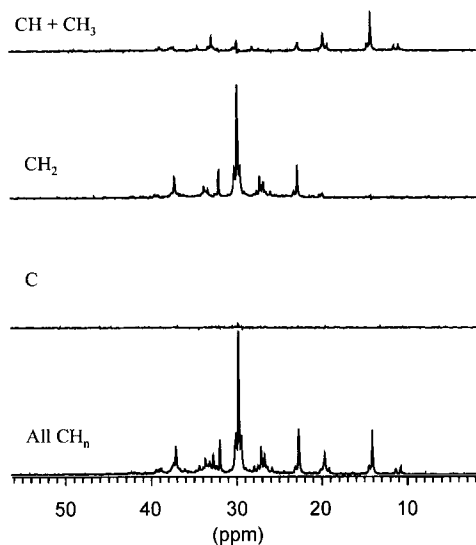


Fig. 4. Conventional ^{13}C -NMR spectrum of B base oil (bottom). The GASPE subspectra are labeled according to the component resonance types as “C”, “ CH_2 ”, and “ $\text{CH} + \text{CH}_3$ ”.

To verify the accuracy of the method in the presence of cyclic aliphatic structure a blend of 33 wt% of squalane and 67 wt% of *n*-butyl-cyclohexane was prepared.

In Fig. 3 the GASPE subspectra of this blend are reported and the CH_n fractions found ($F(\text{CH}) = 0.13$; $F(\text{CH}_2) = 0.71$ and $F(\text{CH}_3) = 0.16$) are exactly the same as the expected ones confirming the reliability of the method.

The GASPE NMR subspectra were obtained for the six base oils: as a general example the B oil subspectrum is shown in Fig. 4. The relative CH_n fractions are obtained and are reported in Table 3.

In Fig. 5 the CH_3 NMR GASPE subspectrum of B base oil as a general example is shown and the methyl peaks are assigned as follows [16, 17] (Table 4).

Table 3. $F(\text{CH}_n)$ fractions of the analyzed base oils.

Base oil	F(C)	F(CH)	F(CH_2)	F(CH_3)
A	0.02	0.16	0.62	0.20
B	0.00	0.14	0.69	0.17
C	0.00	0.13	0.72	0.15
D	0.00	0.14	0.68	0.18
E	0.00	0.08	0.77	0.15
F	0.02	0.07	0.74	0.17

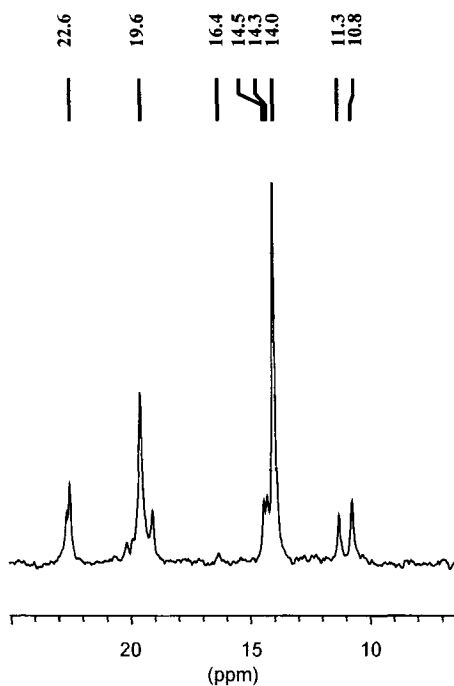


Fig. 5. GASPE CH_3 ^{13}C -NMR subspectra of the B base oil as a typical example.

The molar percentages of the methyls for the six base oils are reported in Table 5.

From these data, it is evident that the non-olefinic base oils are similar: the methyl branches are predominant, while in the PAO and PIO the branches are prevalently longer than C3. Of course inside the former base oils there are some great differences in chemical composition (for instance the content of aromatic compounds – see Table 2).

Table 4. Methyl peak assignment.

Methyl type	^{13}C -NMR chemical shift (ppm from TMS)
$>\text{CCH}_2\text{CH}_3$	10.8
$-(\text{CH}_3)\text{CHCH}_2\text{CH}_3$	11.3
$>\text{CHCH}_2\text{CH}_2\text{CH}_3$	14.5
$-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$	14.3
$-(\text{CH}_2)_n-\text{CH}_2\text{CH}_2\text{CH}_3$ ($n > 1$)	14.0
$-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}<$	15–17
$-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-$	19.6
$\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2-$	22.6

Table 5. Methyl distributions in the average molecular molecule of the analyzed base oils.

	A	B	C	D	E	F
>CCH ₂ CH ₃	0.06	0.10	0.12	0.11	0.00	0.07
-(CH ₃)CHCH ₂ CH ₃	0.12	0.08	0.06	0.07	0.00	0.01
>CHCH ₂ CH ₂ CH ₃	0.01	0.06	0.05	0.07	0.00	0.05
-CH(CH ₃)CH ₂ CH ₂ CH ₃	0.06	0.05	0.07	0.05	0.02	0.02
-(CH ₂) _n -CH ₂ CH ₂ CH ₃	0.32	0.35	0.33	0.25	0.93	0.62
-CH ₂ CH(CH ₃)CH<	0.05	0.04	0.03	0.06	0.05	0.10
-CH ₂ -CH(CH ₃)-CH ₂ -	0.31	0.26	0.30	0.33	0.00	0.13
CH ₃ -CH(CH ₃)-CH ₂ -	0.07	0.06	0.04	0.06	0.00	0.00

To value the number of branches per average molecule (NB) we have determined the average molecular mass of the lubricating oils by VPO and their values are reported as number of carbons (NC) per average molecule in Table 6.

From the knowledge of NC and F(CH₃) the average number of methyls per molecule can be calculated with the following expression:

$$n\text{CH}_3 = F(\text{CH}_3) \cdot \text{NC} . \quad (1)$$

The number of branches (in the hypothesis that they are prevalently linear) is obtained subtracting two (the terminal methyls of the straight aliphatic chain) from the total number of methyls $n\text{CH}_3$ (the resulting number represents the terminal methyl groups of the branches):

$$\text{NB} = n\text{CH}_3 - 2 . \quad (2)$$

The number of aliphatic rings per molecule (NR) is obtained from the number of CH and C atoms exceeding the number of branches:

$$\text{NR} = (2n\text{C} + n\text{CH} - \text{NB}) \cdot 0.5 . \quad (3)$$

The NB and NR values determined for the base oils are reported in Table 6.

Table 6. Average molecular characteristics of the base oils.

Base oil	NC	NB	NR
A	30	4.0	1.00
B	30	3.1	0.55
C	33	3.0	0.67
D	36	4.5	0.28
E	33	3.0	0.51
F	35	3.8	0.65

Table 7. Heats of fusion of the base oils.

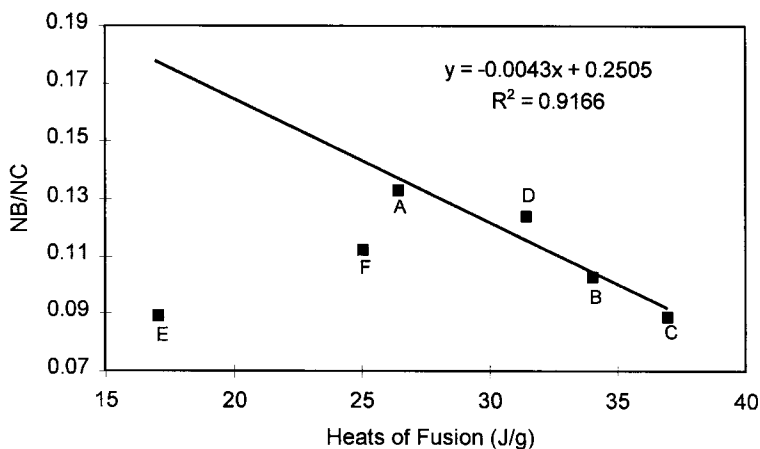
Base oils	ΔH (J/g)
A	26.4
B	34.0
C	36.7
D	31.4
E	17.0
F	25.2

To confirm the reliability of the molecular parameters found we have determined the heats of fusion of the base oils which should be correlated with the presence and the nature of the branches and the cyclic structures. In Table 7 the heats of fusion are reported.

In Fig. 6 the heats of fusion are reported versus the densities of branches expressed as NB/NC.

It is interesting to observe that for base oil of similar aliphatic moieties (the mineral, hydrocracked and hydroisomerized ones) the heats of fusion show a nearly linear dependence on the densities of branches (with $R^2 = 0.9166$), while apparently there is no correlation with the densities of aliphatic rings (Fig. 7). Considering the sum of the densities of branches and aliphatic rings, a better correlation is obtained than the branching densities alone (Fig. 8, $R^2 = 0.9795$).

This result is expected because the heats of fusion are greater for more linear molecules (normal-paraffins have greater heats of fusion than iso- and cyclo-par-

**Fig. 6.** The six base oils heats of fusion as a function of NB/NC (see text).

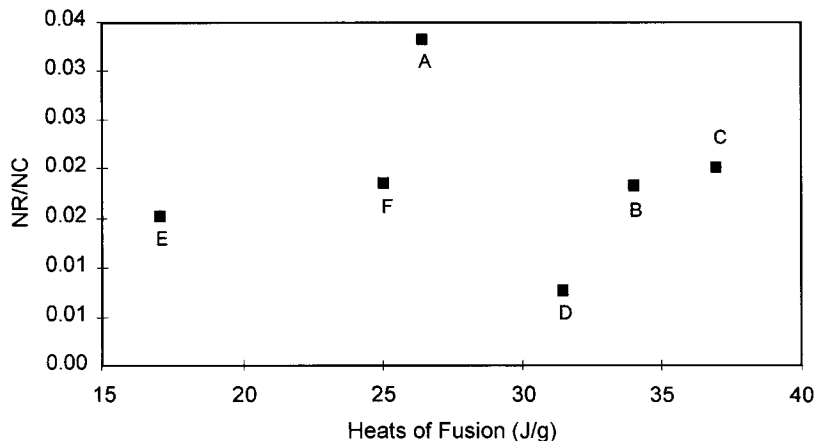


Fig. 7. The six base oils heats of fusion as a function of NR/NC.

affins of the same molecular mass) and confirms the reliability of the value of branches and aliphatic rings determined by NMR.

The much lower heats of fusion found for the PAO and PIO base oils are explained on the basis of the nature of their branches: they are longer than those of the other base oil and prevent the linear aliphatic chains to approach each other arising their crystallization enthalpy.

Considering the pour points of the lubricating base oils versus the densities of branches and cyclic rings (Fig. 9), no clear correlation is evident between them. On the contrary, considering the fractions of methyls on longer chains (more than

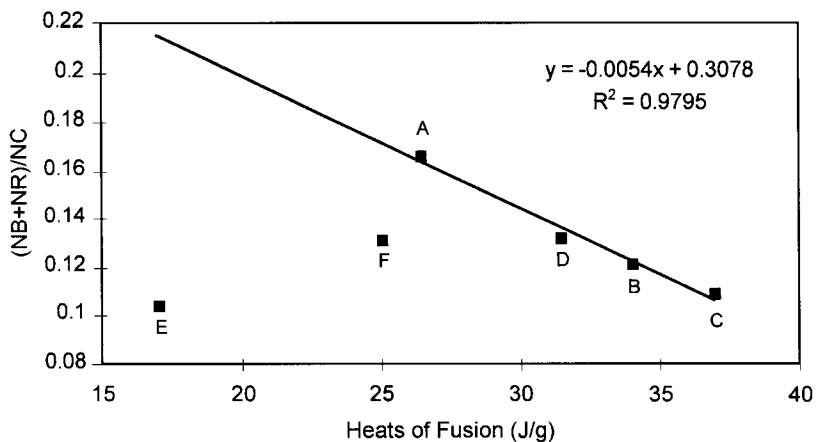


Fig. 8. The six base oils heats of fusion as a function of (NB + NR)/NC.

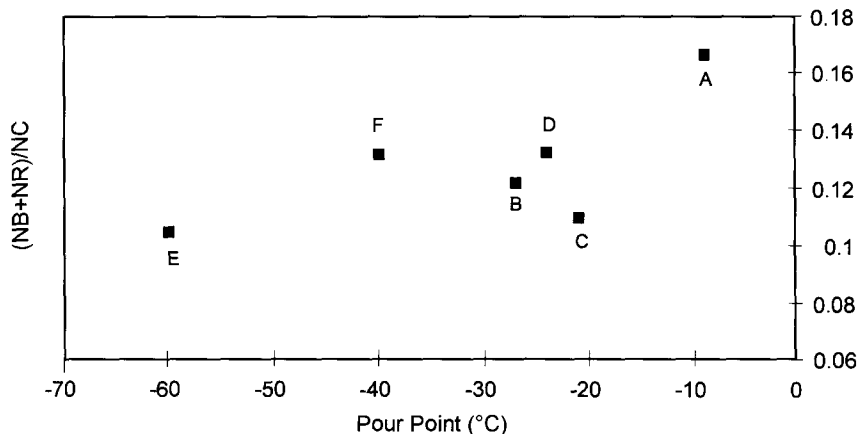


Fig. 9. The six base oils pour points as a function of $(NB + NR)/NC$.

three carbons, the values reported in the row $-(CH_2)_nCH_2CH_2CH_3$, Table 5) there is a quite good linear correlation (Fig. 10) between these values and the base oil pour points, excluding the A base oil (Squared linear correlation coefficient is 0.9951).

So, the correlation of the pour points with the presence of long aliphatic chains is well confirmed for all the synthetic and chemical modified bases (hydrocracked, from waxes hydroisomerization), with the exception of the mineral base, due, very likely, to its origin and preparation (only physical treatments).

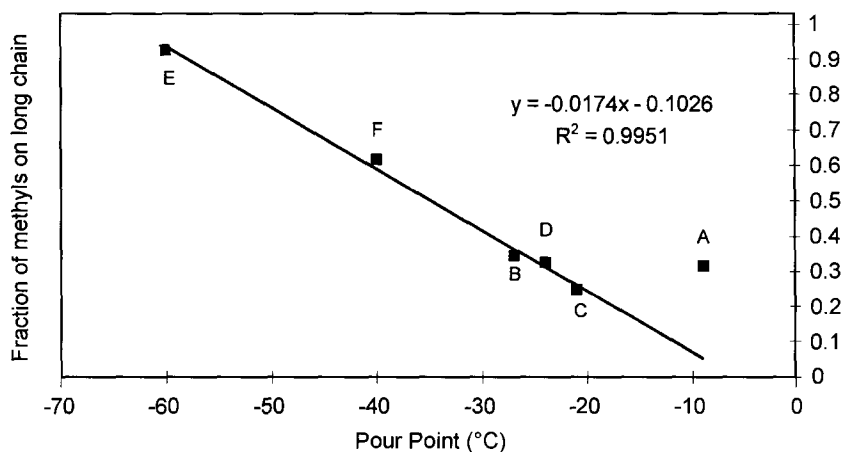


Fig. 10. The six base oils pour points as a function of the fraction of methyl groups on long aliphatic chains.

4. Conclusions

The GASPE spectral editing is a useful technique to determine the nature and the number of branches per average molecule of the base oils. These values are correlated with the physical-chemical properties of the base oils. In particular we have found a nearly linear correlation between the densities of branches with the heats of fusion of the base with the same nature of branches.

Moreover the not olefinic hydrocarburic base oils (mineral, hydrocracked and hydroisomerized) show very similar aliphatic moieties: their branches are prevalently methyls and with the same distribution in length and position along the principal chain.

The synthetic PAO and PIO, vice versa, show prevalently branches longer than C3 which cause their low values of the heats of fusion compared to those of the other oils.

Moreover the base oil pour points resulted to be correlated with the fractions of long chains per molecule more than with the densities of branches, with the only exception of the traditional mineral base oil.

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