Thermal behavior of neopentylpolyol esters

Comparison between determination by TGA-DTA and flash point

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Abstract

In the course of an investigation on the properties of neopentylpolyol esters, we examined their behavior at high temperatures using two different methods: thermogravimetry with differential thermal analysis (TGA-DTA) and measurement of flash point (ASTM D-93). Thermal behavior of the neopentylpolyol esters was found to be related to the length of acyl chain (C9 : 0, C12 : 0, C14 : 0, C18 : 1, C22 : 1) and nature of the polyol (PE, TMP, NPGHP).

We also examined the thermal behavior of the partial esters of pentaerythritol in both, helium and air. The TGA-DTA technique appeared to be a suitable replacement for the flash-point methodology (ASTM D-93), especially for studying the thermal behavior of small amounts of the sample. © 1998 Elsevier Science B.V.

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1. Introduction

Synthetic fatty-acid esters are increasingly employed in synthetic lubricants, which now make up 11% of the lubricant market. The esters of neopentylpolyols are widely used [1] due to their excellent behavior at high temperatures.

In normal operation, lubricants are exposed to a wide range of temperatures, usually on metallic surfaces in the presence of air, where they are subjected to oxidative decomposition and thermal degradation. In general, oxidation predominates due to its lower activation energy.

Thermal degradation is a process that takes place in the absence of oxygen. For the neopentylpolyol esters, it occurs via a radical mechanism giving rise to an alkene and an acid [1]. The esters are thus degraded into low molecular-weight products without formation of polymers [2].

Oxidative decomposition normally occurs in two stages. The first stage produces alkyl radicals which react with oxygen to give peroxides or hydroperoxides. The latter species are unstable at high temperatures and give rise to ketones, aldehydes, acid and alcohols. The limiting step is the primary oxidation reaction, while the second stage is a polymerization. Polymerization is a faster reaction and is influenced by

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the nature of the metal surface [3]. Polymerization produces sludges and an insoluble lacquer. However, a study on trimethylolpropane triheptanoate (TMP C7) showed that this molecule produces few deposits and that any deposits formed tend to be thermally degraded.

Although thermal stability depends on the chemical structure of the substance, stability toward oxidation can be enhanced by the addition of inhibitors [3].

In a study by differential scanning calorimetry (DSC), a modification of differential thermal analysis (DTA), Zeman et al. [4] showed the influence of the nature of the metal surface in contact with the lubricant. Studies on the esters of pentaerythritol and trimethylolpropane demonstrated the formation of some degradation products: acids, ketones, aldehydes, lactones along with simple esters.

In the present study, we compared the thermal behavior of various total esters of neopentylpolyols as a function of the length of the acyl chain (esters of pelargonic C9 : 0, lauric C12 : 0, myristic C14 : 0, oleic C18 : 1 and erucic acids C22 : 1) and the nature of the polyol (pentaerythritol (PE), trimethylolpropane (TMP) and neopentylglycol hydroxypivalate (NPGHP)) under helium (inert gas) or air. The thermal behavior of the different partial esters of erucic acid was then compared to those of the corresponding total esters. Although the C9 : 0 to C18 : 1 fatty acid esters of pentaerythritol and trimethylolpropane have been described in the literature, we are unaware of any reports on esters based on erucic acid and NPGHP. Values for the weight loss of the total esters in air determined by TGA-DTA were compared to the values of flash point measured by a standard method (ASTM D-93). This was designed to compare the high-temperature behavior as determined by a laboratory technique (TGA-DTA) to that used on a pre-industrial scale (flash point).

2. Materials and methods

2.1. Materials

Pentaerythritol (PE, 98%) trimethylolpropane (TMP, 98%) neopentylglycol hydroxypivalate (NPGHP, 98%) and pelargonic acid (C9, 99%) were

supplied by Acros (Noisy Le Grand, France). Erucic acid (C22 : 1, >95%) and the catalyst, *para*-toluene sulfonic acid (*p*-TSA, >99%) were obtained from Fluka (L'Isle d'Abeau Chesnes, France). Myristic (C14, >99%) and lauric acids (C12, >99%) were purchased from Sigma (St Quentin Fallavier, France). The oleic acid (C18 : 1, 72%), as supplied by Prolabo (France), also contained 11% of linoleic acid (C18 : 2).

2.2. Esterification

An aliquot of 25 mmol of alcohol and a stoichiometric amount of fatty acid (50 mmol of fatty acid for NPGHP, 75 mmol for TMP and 100 mmol for PE) are introduced in a 200 ml flask with 40 ml xylene containing 2% *p*-TSA (by weight, with respect to the alcohol). The flask is equipped with a mechanical stirrer (500 rpm), a thermometer and a Dean–Stark trap with cooling system. The mixture is refluxed under nitrogen for 8 h at 170–200°C.

2.3. Purification

At the end of the reaction, all the xylene is evaporated. After cooling, the residual oil is deacidified by an anionic resin to remove the catalyst and excess acid [5]. The different esters are separated on a silica-gel column and eluted with hexane containing increasing amounts of diethyl ether. The purity of the products was determined by TLC using pentane–diethyl ether–formic acid (80 : 20 : 5, v/v) as eluent. The spots were revealed with 2,7-dichlorofluorescein.

2.4. TGA-DTA

The TGA-DTA determinations were carried out on a TG-DTG 92 apparatus (Setaram, Lyon, France). Two different atmospheres were employed: an inert atmosphere under a stream of helium and a 'reactive' atmosphere under a stream of air. The analytical crucibles were made of alumina. The temperature was programmed in two sequences. The first part was a constant temperature of 20°C for 120 s followed by a rise to 500°C at a rate of 10°C/min. Data were acquired every 0.8 s. Samples weighed between 30 and 70 mg.

2.5. Flash point

The flash points were determined according to the standard (ASTM D-93) using the closed cup technique.

3. Results and discussion

Figs. 1 and 2 show two typical thermograms recorded, respectively, under helium and air. Three curves are illustrated:

- TG, thermogravimetric plot (weight loss).
- DTG, first derivative of previous plot.
- DTA, differential thermal plot (heat flow).

The differential curve under helium exhibits an endothermic peak corresponding to thermal decomposition as this reaction absorbs energy from the surroundings.

Under air, the situation is more complex. Apart from the action of oxygen, which gives rise to oxidation reactions reflected by exothermic peaks, the peak was deformed. This has been accounted for by the superimposition of less intense endothermic peaks which correspond to either loss of various volatile decomposition products (evaporation), or a simple thermal degradation.

The significant point on the thermogravimetric curve is the onset of weight loss. Above this temperature, the oil is modified (reaction, evaporation). On the DTA curve, thermal degradation, or degradation due to oxidation, is indicated by the temperature 'onset' which precedes the degradation peak. There was little loss of weight prior to this point, indicating that the esters are relatively non-volatile.

In the next set of experiments, we compared the temperatures of onset of weight loss of the different compounds. On systematic analysis, we could establish relationships between the degradation of esters and the lengths of the acyl chains of the neopentyl-polyol esters and the nature of the polyol.

3.1. Total esters

3.1.1. Under helium

The temperatures of onset of weight loss for the total esters under helium are listed in Table 1. It can be seen that the temperatures ranged from $210°$ to $374°C$, depending on the nature of the alcohol and the associated fatty acid.
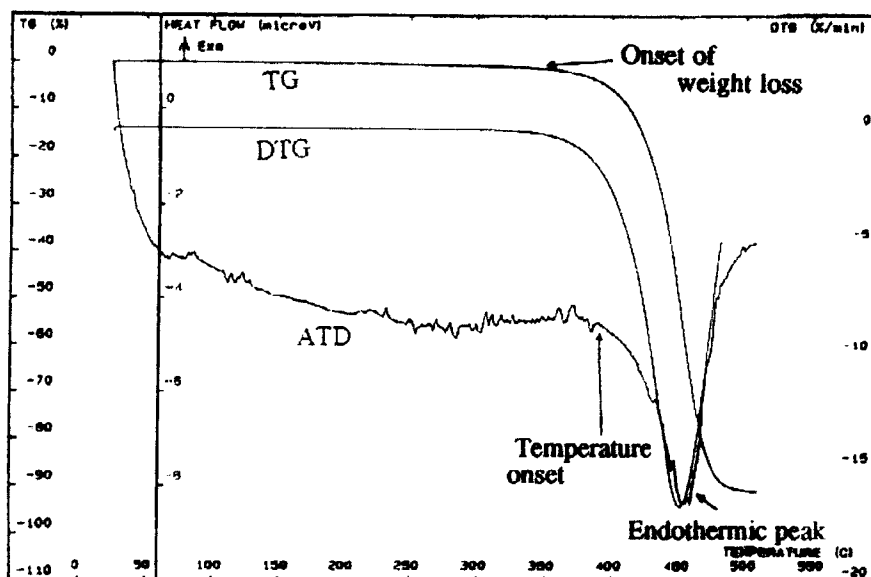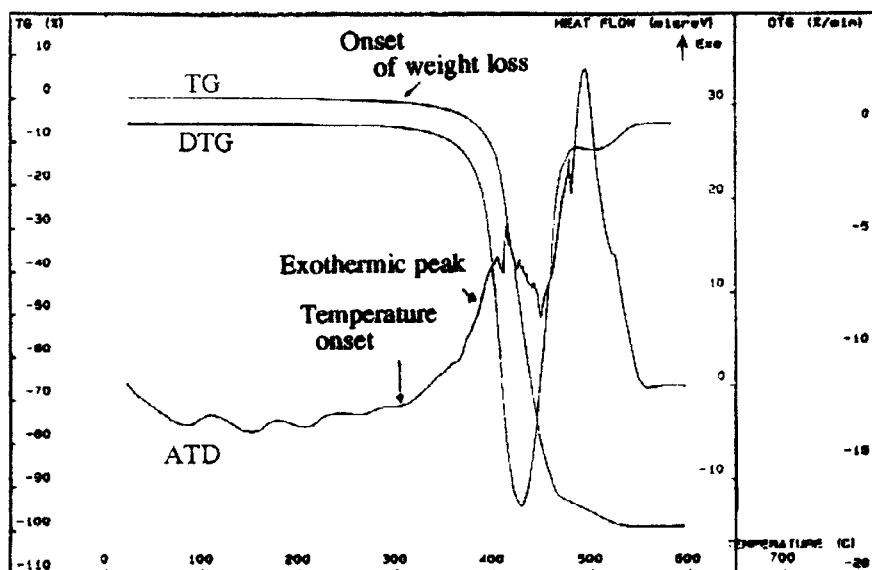

Fig. 1. Thermogram of TMP C22 under helium.

Fig. 2. Thermogram of TMP C22 under air.

Table 1
Temperature of onset of weight loss in °C for the total esters under helium

Length of fatty acid chain	Pentaerythritol	Trimethylolpropane	Neopentylglycol hydroxypivalate
Erucic acid; C22 : 1	374°C	350°C	300°C
Oleic acid; C18 : 1	347°C	312°C	262°C
Myristic acid; C14	312°C	282°C	244°C
Lauric acid; C12	294°C	265°C	231°C
Pelargonic acid; C9	262°C	226°C	210°C

It can be seen from Fig. 3 that there is a linear change in temperature at the onset of weight loss under helium. This value rose with increase in chain length and the number of functional groups on the alcohol. The esters of erucic acid (C22 : 1) were the most stable in every case. In addition, for equivalent chain lengths, the pentaerythritol esters had higher temperatures of onset of weight loss than did the esters of trimethylolpropane or neopentylglycol hydroxypivalate.

The temperatures of onset of weight loss increased with increasing acyl chain length and number of functional groups on the polyol as can be seen from the plots as a function of molar mass. The plot illustrated in Fig. 4 is of the logarithmic type, whose equation could be determined using Cricket Graph software (Macintosh) as:

$$y = 159.54 \ln x - 780.5 \quad r^2 = 0.986$$

where r^2, the correlation coefficient, is close to unity.

It can be seen from Fig. 4 that the temperature of onset of weight loss increased with increase in molar mass. However, a marked increase in molar mass did not lead to a marked increase in temperature of onset of weight loss, which reached a plateau at high molar mass. However, it should be noted that this plot is only valid for comparable compounds, i.e. those in the pure state with linear acyl chains and relatively pure starting fatty acids.

From this plot, the thermal stability, at least under helium, can be predicted for a given molar mass of neopentylpolyol ester derived from a linear chain fatty acid.

PE : y = 189,00 + 8,59x   r2 = 0,993
TMP : y = 149,55 + 9,16x   r2 = 0,990
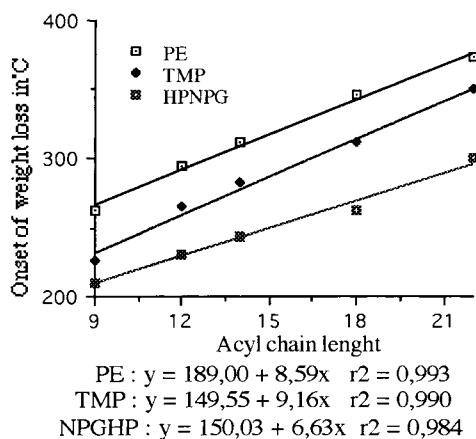NPGHP : y = 150,03 + 6,63x r2 = 0,984

Fig. 3. Onset of weight loss as a function of length of acid chain. Total esters under helium.
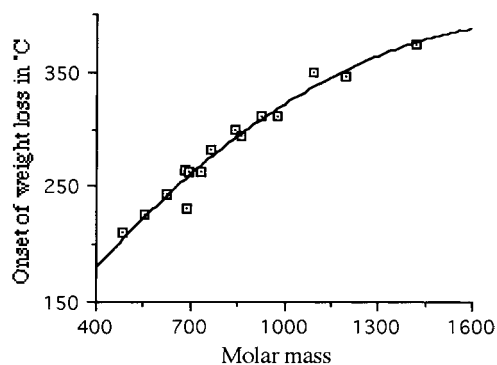

Fig. 4. Onset of weight loss as a function of molar mass. Total esters under helium.

The presence of a double bond did not appear to affect the thermal stability, which only depended markedly on chain length in this series of compounds.

3.1.2. Under air

Lubricants are not normally used in ideal conditions under an inert atmosphere. We, therefore, carried out TGA-DTA analyses under air (20% oxygen). The results for the temperatures of onset of weight loss for the total esters of neopentylpolyols under air are listed in Table 2. It can be seen that the range of temperatures (215–320°C) was below that observed under helium. The compounds were thus more reactive in the presence of oxygen.

From the results presented in Table 2, it can be seen that the chain length had little influence under air. For the same polyol, identical values were obtained for the C18 : 1, C14 : 0, C12 : 0 and C9 : 0 esters, with only the C22 : 1 esters having significantly higher values than the others. Even in the presence of the double bond, it can be seen that the erucates were stable toward oxidation, whereas the analogs with medium or short saturated chains (C14 : 0, C12 : 0 and C9 : 0) were more readily degraded.

The esters of oleic acid (oleates) behaved in a similar way toward the esters with medium or short saturated chains, despite their closer resemblance to the esters of erucic acid. However, it should be noted that the oleic acid employed was not pure (72%) and contained 11% of linoleic acid, which is more sensitive to oxidation. The influence of linoleic acid was even more noticeable in the high-temperature analyses. The presence of two double bonds makes linoleic acid more reactive in air. This is further evidence for the sensitivity of the acyl chains in the neopentylpolyol esters toward oxidation. Contamination with esters of linoleic acid impairs the thermal stability of oleates, giving rise to an overall molecular fragility.

On the differential plots (Fig. 5), a clear peak was observed for all the esters apart from those with erucic acid. Between 220° and 240°C, a small exothermic peak was observed, followed at around 300°C by a series of exothermic-endothermic peaks corresponding to the complete degradation of the compound. This could not be attributed to evaporation of the oil, which

Table 2
Temperature of onset of weight loss in °C. Total esters under air

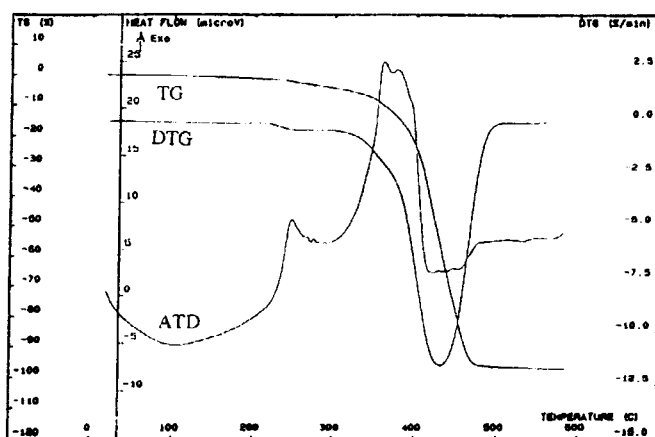| Length of acid chain	Pentaerythritol	Trimethylolpropane	Neopentylglycol hydroxypivalate
Erucic acid; C22 : 1	320°C	307°C	308°C
Oleic acid; C18 : 1	235°C	221°C	233°C
Myristic acid; C14	238°C	220°C	221°C
Lauric acid; C12	232°C	220°C	215°C
Pelargonic acid; C9	235°C	220°C	215°C

Fig. 5. Thermogram of TMP C18 under air.

is characterized by an endothermic peak, comparable to that observed under helium. It was assumed that the esters underwent an initial degradation from the action of oxygen while giving rise to a loss of mass of 2–10%. Complete degradation only took place between 250° and 300°C, depending on the nature of the ester. The total esters of C22 : 1 were the most stable with a temperature of onset of weight loss above 300°C.

3.2. Partial esters

The temperatures of onset of weight loss for the partial esters of C22:1 under helium and air are listed in Table 3, along with those for the total esters. It can be seen that the values in air were lower than those observed under helium. In all cases, values fell with increase in number of residual hydroxyl groups. The hydroxyl site thus appeared to be the most fragile part of the molecule, and governed the stability of the partial esters.

In the more complex pentaerythritol esters, we did not observe a linear relationship (Figs. 6 and 7) between degradation temperature and degree of substitution. The mono- and diesters were less stable than the tri- and tetraesters under both, helium and air. Under air, the temperatures of onset of weight loss of the mono- and dierucates of pentaerythritol were 75° and 80°C, respectively, while for the tri- and tetraerucates of pentaery- thritol they were 300° and 320°C, respectively. Under helium, the values were of a similar order of magnitude as those found under air. The mono- and dierucates of pentaerythritol had temperatures on onset of weight loss of 80° and 100°C, respecti- vely, while the tri- and tetraerucates of pentaery- thritol had values of 318° and 374°C, respectively. The partial and total esters of C22 : 1 exhibited similar behavior under air and helium. Stability was higher in the compounds with a high degree of esterification.

Table 3
Onset of weight loss of partial esters of erucic acid under air and under helium

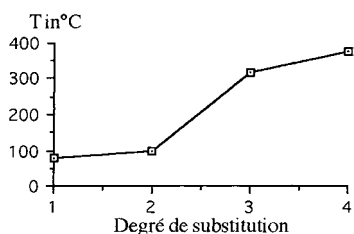| Type of esters	Pentaerythritol esters		Trimethylolpropane esters		Neopentylglycolhydroxypivalate esters	
	under He	under air	under He	under air	under He	under air
Monoester	80	75	90	80	90	82
Diester	100	85	255	165	300	308
Triester	318	300	350	307		
Tetraester	374	320				

Fig. 6. Onset of weight loss as a function of the degree of substitution under helium for esters of pentaerythritol.
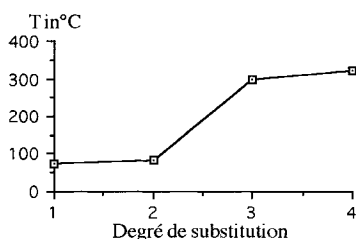

Fig. 7. Onset of weight loss as a function of the degree of substitution under air for the esters of pentaerythritol.

An infrared study on the pentaerythritol esters as a function of temperature provided more information on the molecular interactions of these compounds [6]. We found evidence for intermolecular bonds in the mono- and diesters and for intramolecular bonds in the triester. With a rise in temperature, the intermolecular bonds are dissociated, which affects the stability of the mono- and diesters of C22 : 1. On the other hand, intramolecular bonds in the triester are not broken under these conditions of heating, and the structure of this ester is stabilized by such bonds. The thermal stability of the triester was comparable to that of the total ester, which was the least heat sensitive.

Thermal analysis of the partial esters of erucic acid showed that they were all less stable than the total ester. This explains why partial esters need to be eliminated from lubricants based on neopentylpolyol esters, if they are to be used at high temperatures.

3.3. Flash point

The flash point is the lowest temperature at which a flame will set light to the vapor of the oil or its degradation products. It represents a qualification test and is employed on a pre-industrial scale. In view of the large amounts of compound required, we only tested a single series of total esters. The flash points of the total esters of C22 : 1 were all above 290°C, although the exact temperature could not be determined for technical reasons. However, the flash point of the C9 NPGHP was found to be 216°C.

In a study of numerous total esters of neopentylpolyols, Nutui and al. [7] reported that the flash point rose with increase in the number of carbons in the acyl chain, molar mass and the number of hydroxyl groups in the alcohol. Our results, also supported by our thermal analyses, were in line with these findings. Thermal stability increased with increase in length of acyl chain and with increase in number of functional groups on the polyol.

It should be noted, however, that the results depend on the purity of the starting compounds. The flash points of the oleates of trimethylolpropane and pentaerythritol have been reported at 315° and 320°C, respectively [8]. However, the flash points of the oleates derived from industrial-grade oleic acid produced from tallow are considerably lower (240° and 220°C, respectively).

The values obtained for flash point can be compared to those of the temperature of onset of weight loss in air (Table 4). In both cases, a rise in temperature in the presence of air induced evaporation or degradation of the oil is observed. This is noted as an inflammation of vapor at a lower temperature and the loss of mass on the thermogram. It can be seen from Table 4 that the temperatures of onset of weight loss for the total erucates were above 300°C, while the flash points were above 290°C. The pelargonate hydroxypivalate of neopentylglycol (C9 HP) exhibited a loss of weight at 215°C and a flash point of 216°C. The corresponding oleates exhibited similar thermal behavior.

Table 4
Flash points and temperatures of onset of weight loss under air for the various esters

Molecule	Flash point	Onset of weight loss under air
PE22	>290°C	320°C
TMP22	>290°C	307°C
NPGHP22	>290°C	308°C
NPGHP9	216°C	215°C
PE18	220°C	235°C
TMP18	240°C	220°C

Based on the same principle, these two techniques give comparable results. The laboratory-scale thermal analysis method could, thus, replace measurement of flash point for evaluation of the thermal stability of lubricants. The thermal analysis method is fast and requires small amounts of sample. The TGA/DTA method, therefore, appears to be well-suited for prediction of the thermal behavior of new lubricants.

4. Conclusion

The TGA-DTA technique was employed to analyze the thermal behavior of esters of neopentylpolyols under both, an inert (helium) and oxidizing (air) atmosphere. The results showed that the thermal stability depended largely on the chemical structure of the acyl chain of these esters. Monounsaturation and length of acyl chain and a high degree of substitution of the polyol were all found to contribute to good thermal stability. The esters of erucic appeared to be the most stable at high temperatures under both, helium and air. This new series of esters, based on erucic acid, thus shows considerable promise. Knowledge of the thermal stability of the compound can help evaluate the quality and resistance of the different structures, either alone or in the presence of an antioxidant. The TGA method can also throw more light on the reactions leading to weight loss with rise in temperature (evaporation, oxidation, thermal decomposition, polymerization, etc.).

The domain of application of a lubricating oil is frequently governed by its thermal behavior. Thermal analysis, using the TGA-DTA technique, could thus replace the standard flash-point method (ASTM D-93) for evaluating thermal behavior. We found that the flash points were close to the temperatures of onset of weight loss under air, as determined by the TGA-DTA

method. This method can also be used in the laboratory to evaluate the thermal behavior of small amounts of compounds, such as partial esters as well as mixtures of total and partial esters [9]. Thermal analysis is well-suited for establishing the thermal properties of neopentylpolyol esters. It was found to be valid for characterizing known esters and a new series prepared from erucic acid.

Acknowledgements

References

[1] V. Eychenne, Z. Mouloungui, A. Gaset, O.C.L. 3(1) (1996) 57–63.
[2] A. Ali, F. Lockwood, E.E. Klaus, J.L. Duda, E.J. Tewksbury, ASLE Trans. 22(3) (1979) 267–276.
[3] S. Gunsel, E.E. Klaus, J.L. Duda, Lubr. Eng. 44(8) (1988) 703–708.
[4] A. Zeman, R. Stuwe, K. Koch, Thermodyn. Acta 80 (1984) 1–9.
[5] V. Eychenne, Z. Mouloungui, A. Gaset, J. Am. Oil Chem. Soc., accepted for publication.
[6] V. Eychenne, Z. Mouloungui, A. Gaset, J. Am. Oil Chem. Soc. 75(2) (1998) 293–299.
[7] R. Nutiu, M. Matie, M. Nutiu, J. Synth. Lubr. 7 (1990) 145–154.
[8] H. Kohashi, Application of fatty acid esters for lubricating oil, in: T.H. Applewhite (Ed.), World Conference on Oleochemical into the 21st Century, American Oil Chemists Society, Champaign, Illinois, 1990, p. 243–250.
[9] V. Eychenne, Thèse INP Toulouse (1977), No. C1291 Synthèse des esters de néopentylpolyols, Corrélations structures/Propriétés tribologiques/Performances en lubrification.