

# Oligoalkylnaphthenic (C<sub>6</sub>-C<sub>12</sub>) Oils Obtained in the Presence of Ti-Containing Ionic-Liquid Catalysts

Akif Hamid Azizov, Reyhan Valy Aliyeva, Khayala Haydar Asgerova\*

The Y.H. Mamedaliyev Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences,  
Baku, Azerbaijan  
Email: \*xayala\_550@rambler.ru

Received August 5, 2013; revised September 5, 2013; accepted September 12, 2013

Copyright © 2013 Akif Hamid Azizov *et al.* This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

## ABSTRACT

In this present paper, the result of C<sub>6</sub>-C<sub>12</sub>  $\alpha$ -olefins oligomerization in the presence of recyclable chloroaluminate type ionic-liquid catalysts and their combination with Ti-containing complexes is presented. By different methods of analysis the composition and structure of oligoalkylnaphthenic products obtained in the presence of ionic-liquid catalysts and Ti-containing modifiers have been studied.

**Keywords:** Ionic Liquid; Oligomerization; PAO

## 1. Introduction

The continued use of large quantities of organic solvents as liquid media for chemical reactions, extractions and formulations is a major problem in nowadays chemical industry. Here E-factor, as it was defined by Roger Sheldon, is the environmental factor of a process, e.g. the ratio (by weight) of the by-products to the desired product(s). As can be seen, the oil refining and bulk chemicals industries are the least polluting industries, while the fine chemicals and pharmaceutical companies, using inefficient and dirty processes, albeit on a much smaller scale, are polluting the environment severely. In addition to the problematic volatility of these solvents, they often present additional risk due to toxicity and/or flammability [1]. Thus, the discovery of surrogates to traditional organic solvents which offer reduced environmental impact and safer processes is of great importance.

J. D. Holbrey and K. R. Seddon consider four main alternate strategies for this: solvent-free synthesis, the use of water, the use of supercritical fluids as solvents and the use of ionic liquids as solvents.

The option of the use of ionic liquid as solvents seems to be one of the most promising methods in green chemistry. The unique peculiarities of low temperature ionic liquids such as non-volatility, non-flammability, low melting points, high thermal stability in a wide temperature range, relatively low viscosity, inexpensivity and diver-

sity to manufacture and so on, have attracted interests of investigators from industrial and academic research centers from all around the world. They are highly solvating liquids, composed of bulky cations and anions, which dissolve many organic and inorganic substances. In the last few years there appeared a lot of papers and patents, devoted to preparation methods, solvent properties and application of ionic liquids as the solvents in different processes. Some of them have been overviewed in [1-10].

Low temperature ionic liquids are widely investigated as replacement for environmentally hazardous volatile organic solvents in the processes of organic synthesis and petrochemistry.

They have been used primarily as replacements for conventional media in green chemical processes or as solvent catalysts. The first use of ionic liquids in homogeneous catalysis was reported in 1990 for dimerisation and polymerization reactions [11,12]. Since then, a rapidly growing number of transition metal catalysed reactions have been described in various ionic liquids.

Ionic liquids are often called “green solvents”, and indeed the link between ionic liquids and green chemistry is mainly related to the characteristic of low volatility. The review presents C<sub>6</sub>-C<sub>12</sub>  $\alpha$ -olefins oligomerization in the presence of recyclable chloroaluminate type ionic-liquid catalysts and their combination with Ti-containing complexes. Many of methods of analysis are used to study the composition and structure of oligoalkylnaphthenic products.

\*Corresponding author.

## 2. Experimental

All operations on the catalyst synthesis and oligomerization reactions were performed in an inert gas (nitrogen, argon) atmosphere using anhydrous solvents (benzene, toluene) and freshly distilled C<sub>6</sub>-C<sub>12</sub>  $\alpha$ -olefins.

$\alpha$ -olefins—before the use was dried over calcinated Al<sub>2</sub>O<sub>3</sub> or CaCl<sub>2</sub> and purified by distillation in atmospheric pressure.

Waterless AlCl<sub>3</sub> was stored in an inert atmosphere in the hermetic vessels.

Diethylamine hydrochloride (DEAHC) used for complex ammonium salts preparation were purified by distillation at atmospheric pressure or by recrystallization.

Chloroaluminate ionic—liquids were prepared by interacting AlCl<sub>3</sub> with the corresponding complex ammonium salt taken at molar ratios 1.5 - 2.1.

Synthesis of the ionic-liquid catalytic systems and also oligomerization of  $\alpha$ -olefine in their presence were carried out in the thermostated dried up glass reactor in the atmosphere of dry nitrogen or argon.

With that end in view the reactor was preliminary carefully vacuumized at warming up in a nitrogen current before preparation of the complex catalyst. Then after cooling to a room temperature the corresponding amine were entered into it.

The needed quantity of AlCl<sub>3</sub> was added to the obtained complexes in a nitrogen current at intensive mixing. Catalyst preparation was accomplished at 30°C -

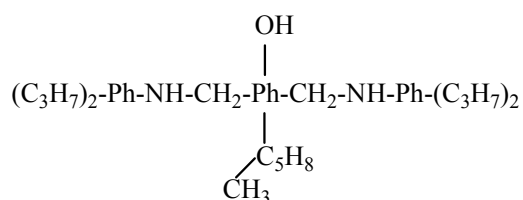
35°C during 10 - 30 minutes.

The ionic liquids obtained represented themselves viscous liquids at room temperature with a yellowish shade.

After termination of chloroaluminate ionic-liquid catalysts (ILC) synthesis  $\alpha$ -olefin was introduced into the reactor at mixing through a drop funnel.

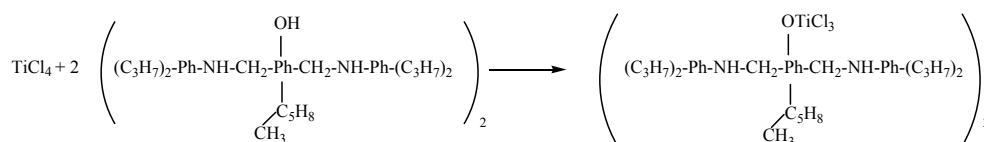
TiCl<sub>4</sub> was applied in the form of a mobile colourless liquid smoking strongly on air. Molecular weight (M) 189.71, density (D<sup>25</sup>) 1.726, fusion temperature (T<sub>m</sub>)-23°C, boiling temperature (T<sub>b</sub>) 135.8°C (760 mmHg).

2,6-di-(2',6'-diisopropyl-1-aminomethyl)-4-(1-methylcyclopentile)-phenol (M = 554, T<sub>boiling point</sub> = 205 - 207°C, T<sub>melting point</sub> = 91°C) has been prepared using the known method by interaction of para-(1-methylcyclopentyl)-phenol

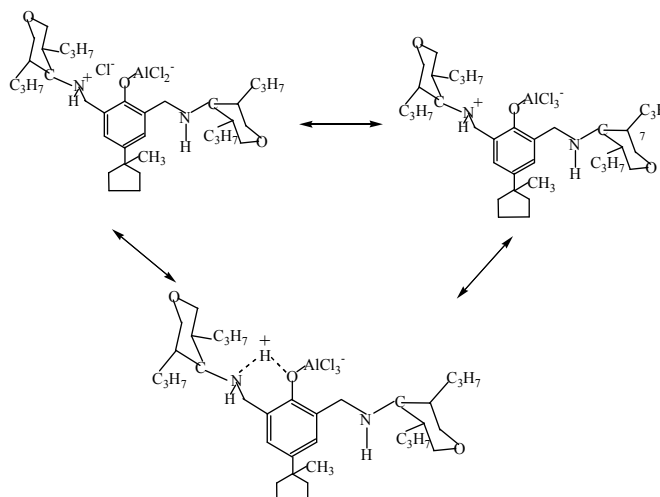


with formaldehyde and 2,6-diisopropylaniline according to Mannich reaction.

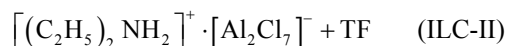
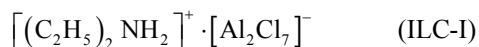
The titanium-phenolate complex (TF) was synthesized by the simple one-step method of interacting 2,6-di-(2',6'-diisopropyl-1-aminomethyl)-4-(1-methylcyclopentile)-phenol with TiCl<sub>4</sub>:



HCl released from the reaction was bound to the amine functionality of the phenolic compound in situ and remained as a part of the formed Ti-containing complex, which, after removal of the solvent, was represented as the brown colored powder, supposedly, sof zwitterionic type complex of the following formula:



The following ionic-liquid catalysts were prepared by this method:



For the preparation of TF was dissolved in ILC-I at the weight ratio TF:ILC-I = 0.001:1.

The experiments on oligomerization were conducted at the temperatures 60°C over 3 h with intensive agitating of reaction mass by a electromagnetic stirrer. After the termination of oligomerization the reaction products were separated from the catalyst by washing off it with 10% solution of NaOH and then by the distilled water till the neutral reaction or by decantation. After drying the unreacted monomer was distilled off from the obtained oil in vacuum and synthetic oil fraction having b.p. 250 - 350°C or >350°C was isolated.

In case of application in the quality of ionic-liquid catalyst of the catalytic system, prepared on aluminum chloride basis, the oligomerization process was conducted at the fusion temperature of the specified ILC. In this case, upon termination of reaction the received reaction mixture was divided into two layers at cooling: the bottom layer represented ILC layer, the top layer – the oligomerizate layer. After separation of ILC from oligomerizate by decantation it was stored in an inert gas atmosphere for further reusing it repeatedly.

Oligomerization of C<sub>6</sub>-C<sub>12</sub> α-olefins was carried out with application of the synthesized ionic-liquid catalytic systems in quantities, in which AlCl<sub>3</sub> content was within 2% mass, counted on the olefin. The received results are presented in **Table 1**.

Oligomerization of C<sub>6</sub>-C<sub>12</sub> α-olefins was conducted in the presence of ILCS-I and ILCS-II. A way of preparation of ILCS, a course of carrying out of the oligomerization processes and the analysis methods.

The results of researches on oligomerization of α-olefin in the presence of ILCS-I and ILCS-II at 60°C, iden-

tical concentration of catalyst (0.2% AlCl<sub>3</sub> masses, counted on olefin) are resulted in **Table 1**.

Apparently, the total amount of ILCS-I and ILCS-II in all cases of oligomerization makes 6% of mass., and a yield of oligomer amounts 85 - 103.92 gr oligomer/gr Al × hour, 77.1 - 90.3 × 10<sup>3</sup> gr oligomer/gr Ti × hour, correspondingly. After the end of reaction, oligomerizate easily separates from catalyzate because of diphasic character of the process. ILCS is kept in the form of uncolored bed in an inert medium. A yield of products, within 3 h. amounts 68% - 85%.

### 3. Methods of Analysis

Oligomerization products were analyzed by exclusion chromatography, DSC, IR- and PMR-spectroscopy.

Molecular-weight distribution (MWD) of the obtained products was studied by size exclusion chromatography method using high performance “Kovo” (Czech Republic) liquid chromatograph with a refractive index detector. Two 3.3 mm - 150 mm columns packed with the “Separon-SGX” stationary phase with a particle size of 7 mm and a porosity of 100 Å were used. Dimethylformamide was used as an eluent (flow rate 0.3 ml/min, temperature 20 - 25°C). A calibration plot of log M versus VR in the range M = 2 - 100 - 102 was obtained using polyethylene glycol standards and transformed to the common dependence of fraction (%) of chains from their molecular weights (**Figure 1**). Calculations of the average molecular weights and MWD characteristics were made from the data of size exclusion chromatographic analysis in accordance with the procedure described in [14]. Average molecular weights (M<sub>w</sub> and M<sub>n</sub>) were calculated using the following formulas:

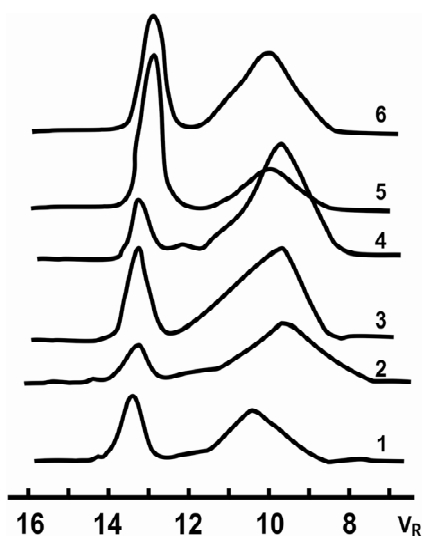
$$M_w = \sum M_i \omega_i, \quad M_n = 1 / \sum \omega_i / M_i$$

where M<sub>i</sub> is the molecular weight, corresponding to the i<sup>th</sup> slice of the chromatogram; ω<sub>i</sub> is the area fraction of the i<sup>th</sup> slice.

**Table 1. Oligomerization of α-olefin depending on composition of ILCS [Conditions: aminophenol: TiCl<sub>4</sub> = 1:1 mol., medium: argon].**

№	Monomer	ILC	[Al], mol/l,	[Ti], mol/l·10 <sup>-4</sup>	Ti/Al, mol·10 <sup>-4</sup>	Yield*		
						qr of oligomer /qr Al × hour	qr of oligomer /qr Ti-hour × 10 <sup>3</sup>	mass. %
1	C <sub>6</sub> **	I	0.19	—	—	85	—	68
2		I	0.2	—	—	87	—	70
3	C <sub>7</sub>	II	0.2	1.3	6.8	93	79,7	75
4		I	0.2	—	—	88	—	71
5	C <sub>8</sub>	II	0.2	1.3	6.8	91	78.5	73.5
6		I	0.22	—	—	89	—	72
7	C <sub>10</sub>	II	0.22	1.5	6.8	90	77,1	80
8		I	0.22	—	—	100.25	—	82
9	C <sub>12</sub>	II	0.22	1.4	6.8	103.92	90.3	85

\*Yield after 3 h. \*\*Oligomerizatssion conditions: t = 25°C; time = 45 min; amount of ILC = 8 wt% of 1-hexene [13].



**Figure 1.** Exclusion chromatograms of oligoalkylnaphtenic ( $C_6$ - $C_{12}$ ) fraction obtained in the presence of ILCS-I and ILCS-II.

DSC analysis was carried out on a Thermoelectron Q-20 Differential Scanning Calorimeter, USA (Joint Grant of NASA and CRDF no. SIP-03), at a heating rate of  $10^\circ\text{C}/\text{min}$  in the air or nitrogen atmosphere.

IR-spectroscopy analysis of the samples was performed on a Spectrum BX, FT-IR system "Perkin-Elmer" (USA) in the range  $650 - 4400 \text{ cm}^{-1}$ .

PMR spectra were recorded on a Bruker pulsing Fourier spectrometer (Germany) operating at the frequency of 300 MHz and at room temperature. Deuterated acetone was used as a solvent. The relative amount of protons in various structural fragments was calculated by the integration of the corresponding resonance absorption bands.

## 4. Result and Discussion

### 4.1. Molecular Weight Characteristics of the Oligomers

The results of exclusion chromatographic analysis of  $C_6$ - $C_{12}$   $\alpha$ -olefins oligomers ( $Fr > 350^\circ\text{C}$ ) are presented on **Figure 1**. As is seen from **Table 2**, the oligomerization products of dodecene-1 received in the presence of ILCS-I and ILCS-II have the MM indexes within the limits— $M_w = 1560 - 6890$ ,  $M_n = 1400 - 5300$ , where MMD coefficient changes within  $M_w/M_n = 1.11 - 1.19$ . Anyway in each system the received MMD indexes change in the narrow limits.

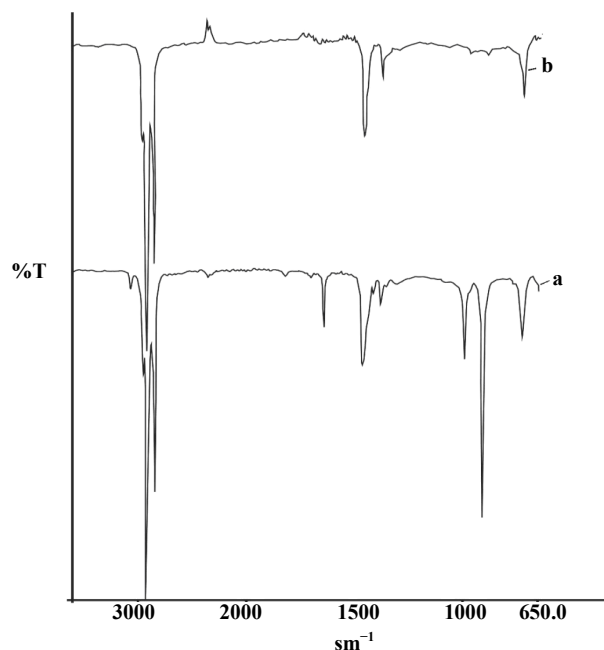
### 4.2. Structure

The received oligomers have also been investigated by IR-spectroscopy (**Figure 2**). In the IR spectrums of initial monomer— $\alpha$ -olefin the absorption band was observed at

**Table 2.** Molecular mass indexes of oligolefin fractions received in the presence of ILCS.

N <sup>o</sup>	Monomer	ILCS	$M_w$	$M_n$	$M_w/M_n$
1	$C_6^*$	I	690	640	1.08
2	$C_7$	I	1560	1400	1.11
3		II	3770	2385	1.16
4	$C_8$	I	3000	2500	1.2
5		II	3900	3700	1.05
6	$C_{10}$	I	4450	3740	1.19
7		II	5180	4540	1.14
8	$C_{12}$	I	4820	4310	1.12
9		II	6890	5300	1.3

\*Oligomerization conditions:  $t = 25^\circ\text{C}$ ; time = 45 min; amount of ILC = 8 wt% of 1-hexene.



**Figure 2.** IR spectrum of dodecene-1 (a) and of oligododecene fraction (b), produced in the presence of ILCS-I.

$721 \text{ cm}^{-1}$ , responsible for the pendular fluctuations of the methylene groups ( $-\text{CH}_2-$ )<sub>n</sub> with  $n > 4$ . There are also the bands of deformation at  $1377.1 \text{ cm}^{-1}$  and valence vibrations at  $2853.5 \text{ cm}^{-1}$ , characteristic for methyl groups ( $-\text{CH}_3$ ). Deformation absorption bands at  $1465.64 \text{ cm}^{-1}$  and valence vibrations bands at  $2922.7 \text{ cm}^{-1}$  correspond also to the methylene groups ( $-\text{CH}_2-$ ). Except the listed absorption bands, there are in the spectrum the deformation bands at  $1300.30 \text{ cm}^{-1}$  and the valence vibration bands at  $2955.60 \text{ cm}^{-1}$ , characteristic for  $-\text{CH}$  groups. Besides, there are the absorption bands at  $908.3 \text{ cm}^{-1}$ ,  $992.05 \text{ cm}^{-1}$  corresponding to deformation fluctuations of the end vinyl groups. And also the bands with maxima at  $1821.1 \text{ cm}^{-1}$  are displayed, responsible for an overtone

of nonplanar deformation fluctuations of the end vinyl groups. Absorption band with a maximum at  $1641.6\text{ cm}^{-1}$  is characteristic for the valence vibrations of C=C bonds of nonsaturated hydrocarbons, and at  $3076.4\text{ cm}^{-1}$  for the valence vibrations of -CH = group in an alkene molecule.

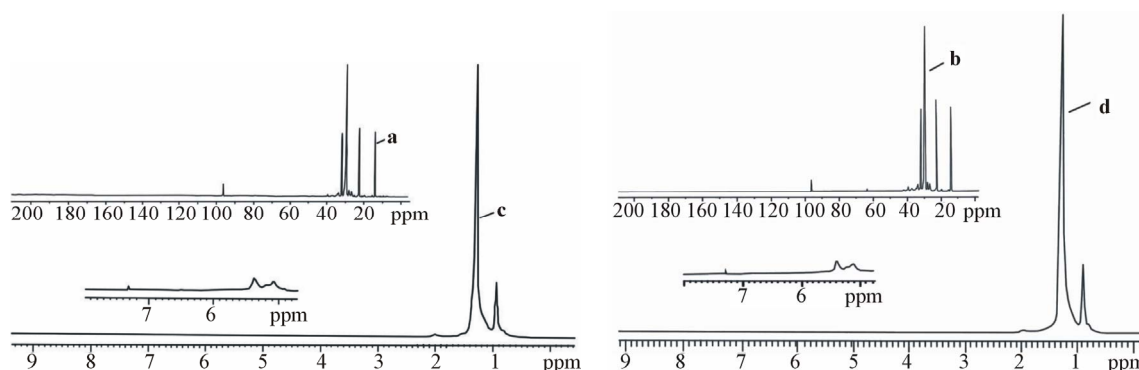
Analysis of the IR spectrums of C<sub>6</sub>-C<sub>12</sub> oligoalkyl fraction (OAF) received in the presence of ILCS has shown that intensity of absorption bands in them with maxima at  $908.3\text{ cm}^{-1}$ ,  $992.\text{ cm}^{-1}$ ,  $1641.6\text{ cm}^{-1}$ ,  $1821.4\text{ cm}^{-1}$ , characteristic for nonsaturated hydrocarbons is much less than in the initial monomer. There are in the spectrums the absorption bands at  $980.3\text{ cm}^{-1}$ ,  $1020.2\text{ cm}^{-1}$ , characterizing the oscillating motions of the carbon atoms in the naphthenic rings, and at  $900.2\text{ cm}^{-1}$ , responsible for hydrogen atom of the isolated naphthenic ring [15,16].

For  $\alpha$ -olefins and oligoalkyl fraction, received in the presence of ILCS were calculated the optical densities of the bands characterizing oscillating motions of paraffinic, naphthenic, nonsaturated fragments. The obtained data

are presented in **Table 3**.

The results of definition of structure oligoalkylfraction synthesized in the presence of ILCS (**Tables 4, 5 and Figure 3**) by NMR-spectroscopy method have also confirmed the data of the IR-spectral analysis. The PMR-SPECTRA of oligoalkylfraction samples, received in the presence of ILCS-I and ILCS-II, are also characterized by the presence of the resonance absorption bands of the protons of methyl (CH<sub>3</sub>-) (0.89 - 0.98 ppm) and methylene (-CH<sub>2</sub>-) (1.28 ppm) groups, and also resonance absorption bands in the field of 1.50 - 1.80 ppm, corresponding to chemical shifts of the protons in the naphthenic frames.

After strong amplification (16 times) the signals in the field of 4.8 - 5.5 ppm, corresponding to nonsaturated structures, very weak absorption bands that specified the insignificant presence of olefinic linkages have been found. At significant intensifying of resonance absorption by accumulation in the PMR spectra of oligodecene



**Figure 3.** <sup>13</sup>C NMR (a, b) and PMR (c, d) spectra of oligododecene fraction produced in the presence: ILCS-I (a, c) and ILCS-II (b, d).

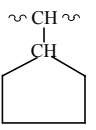
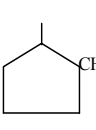
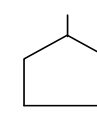
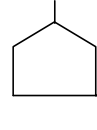
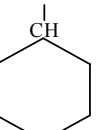
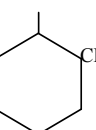
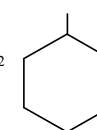
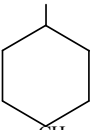
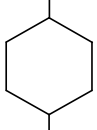
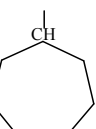
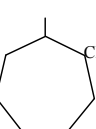
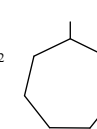
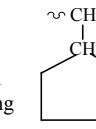
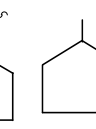
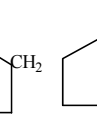
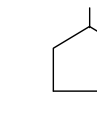
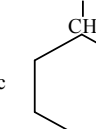
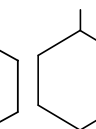
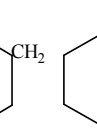
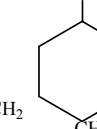
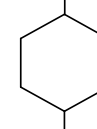
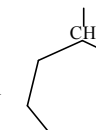
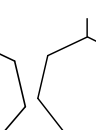
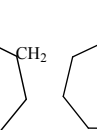
**Table 3.** Optical densities calculated from IR spectra.

Sample	ILCS	D <sub>920</sub>	D <sub>1000</sub>	D <sub>1650</sub>	D <sub>900</sub>	D <sub>980</sub>	D <sub>720</sub>	D <sub>1380</sub>
C <sub>10</sub>	-	1.9138	1.1357	0.5916	-	-	0.4367	0.4225
	II	0.0512	-	0.0649	0.0939	0.0792	0.6532	0.8159
C <sub>12</sub>	-	1.9243	1.1416	0.6232	-	-	0.5441	0.5093
	I	0.0435	-	-	0.0550	0.0669	0.5819	0.7202
	II	0.1684	0.0792	0.0550	0.0918	0.0918	0.5819	0.6232

**Table 4.** Structural parameters determined from PMR spectral data of dodecene-1in the presence of ILCS oligomerization products.

ILCS	Distribution of hydrogen atoms in structural fragments, %				
	-CH = CH <sub>2</sub> (5.0 - 5.3 ppm) -CH = CH- (5.3 - 5.5 ppm)	CH <sub>2</sub> at double bond (1.90 - 2.15 ppm)	CH at 5 - 7 naphthenic ring (1.45 - 1.80 ppm)	β CH <sub>2</sub> , in the chain (1.05 - 1.45 ppm)	Terminal CH <sub>3</sub> group (0.50 - 1.05 ppm)
I	0.25	2.03	3.19	75.48	17.93
II	0.39	2.65	5.35	72.41	16.18

**Table 5. Assignment of the signals in the  $^{13}\text{C}$  NMR spectra of dodecene-1 oligomerization products.**

<i>ILCS-I</i>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>
Chain	CH <sub>3</sub> - 14.265	-CH- 29.834	-CH <sub>2</sub>	-CH <sub>2</sub> - 29.499	-CH <sub>2</sub> - 32.045	-CH <sub>2</sub> -	-CH <sub>2</sub> -	-CH <sub>2</sub> - 32.045	-CH <sub>2</sub> - 29.499	CH <sub>2</sub> -	-CH <sub>2</sub> - 22.793	CH <sub>3</sub> 24.265
5-membered naphthenic ring	 28.277	 --	 26.826			 19.879						
6-membered naphthenic ring	 28.277	 39.557	 26.826	 26.826			 22.793					
7-membered naphthenic	 34.899	 37.205	 26.826									
<i>ILCS-II</i>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>
Chain	CH <sub>3</sub> - 14.229	-CH- 29.845	-CH <sub>2</sub>	-CH <sub>2</sub> - 29.509	-CH <sub>2</sub> - 32.053	-CH <sub>2</sub> -	-CH <sub>2</sub> -	-CH <sub>2</sub> - 32.053	-CH <sub>2</sub> - 29.509	-CH <sub>2</sub> -	-CH <sub>2</sub> - 22.793	-CH <sub>3</sub> 14.229
5-membered naphthenic ring	 28.272	 --	 26.820			 19.838						
6-naphthenic ring	 28.272	 39.547	 26.820	 26.820			 22.793					
7-membered naphthenic	 34.856	 37.222	 26.820									

weak absorption bands of protons of the CH = CH<sub>2</sub> methylene groups (at 5.0 - 5.5 ppm), and of vinylic CH = CH groups at 5.7 - 5.7 ppm) are observed also [17].

Research of the structural parameters of C<sub>6</sub>-C<sub>12</sub>  $\alpha$ -olefins oligomerization products, specify passing of the

process with formation of the oligomers enriched with the fragments of (iso) paraffinic and naphthenic nature which concentration changes within 96.3 - 97.3 and 2.4% - 3.0% mass depending on the composition of catalytic system. Accordingly, concentration of the fragments con-

taining multiple bonds make only 0.3% - 1.0% mass., which is much more low than in initial olefine (Table 5).

This fact once again obliquely testifies to passing of ring formation in the last part of a growing chain. With growth in the length of an alkyl radical in the olefin molecule the probability of bigger naphthenic ring formation increases.

The results of IR-, PMR and NMR spectral analyses have shown identity of frames of all investigated oligoalkylnaphthenic samples, synthesized in the presence of chloroaluminate ILCS. Though, the weak absorption bands observed in both spectra, characterizing multiple bonds, testify to the presence in the synthesized products of the trace amounts of nonsaturated fragments.

### 4.3. Some Physical and Chemical Properties Oligoalkylnaphthenic Oils

Some physical-chemical indexes of oligoalkylnaphthenic product, produced in the presence of ILCS-I and ILCS-II, have also been estimated. The results are presented in Table 6. The values of viscosity index (VI) have been calculated in accordance with GOST 25371-97. Physical - chemical properties of the synthesized oligoalkylnaphthenic product were defined according to the procedures [18,19].

From the data of Table 6 it is evident that the samples of the synthesized oligoalkylnaphthenic oils have low density values, high viscosity and viscosity index ( $\geq 108$ ), low freezing point ( $-33^{\circ}\text{C}$  -  $-45^{\circ}\text{C}$ ), high ignition temperature ( $\geq 172^{\circ}\text{C}$ ), good antioxidative stability, detergency and low vapor ability, do not contain in their composition sulphurous compounds and metal-complexes.

Thus the results of conducted researches show that upon oligomerization of  $\text{C}_6\text{-C}_{12}$   $\alpha$ -olefins with participation of the chloroaluminate type ionic liquid catalysts may be synthesized the oligomeric molecules having predominantly hybridized paraffinic-naphthenic struc-

tures, free of unsaturated fragments. This may favor to use them as a component for preparation of synthetic and semisynthetic base oil compositions without use of hydrogenation step or providing it in a mild condition.

With that end in view hydrogenation of oligododecenenaphthenic oil was conducted using industrial Ni/Cr/Pd catalyst at  $P = 30 \text{ atm.}$ ,  $T = 120^{\circ}\text{C}$ , time = 4 h. It has been found that even in that comparatively hard conditions the VI indexes of the tested samples do not change practically after hydrogenation (VI = 159 before, and 158 after hydrogenation). But some destruction of the high molecular weight molecules takes place during hydrogenation.

In the DSC curves the shift in the position of high molecule peak at  $V_R = 10 - 12$  to  $V_R = 14$  takes place. After hydrogenation the share of the oligomer molecules with  $V_R = 14$  decreases. The destruction process leads to some changes in the thermal indexes of oligomerization product oligododecenenaphthenic defined by DSC method (Termoelectron Corporation Q-20, USA). After hydrogenation of oligododecenenaphthenic the *heat flow value* (Wt/g) *decreases a little* (Figure 4). The hydrogenated product characterizes by less induction period and more complicated course of its oxidation (Figure 5), which confirms occurrence of destruction process taken place in the hydrogenation conditions.

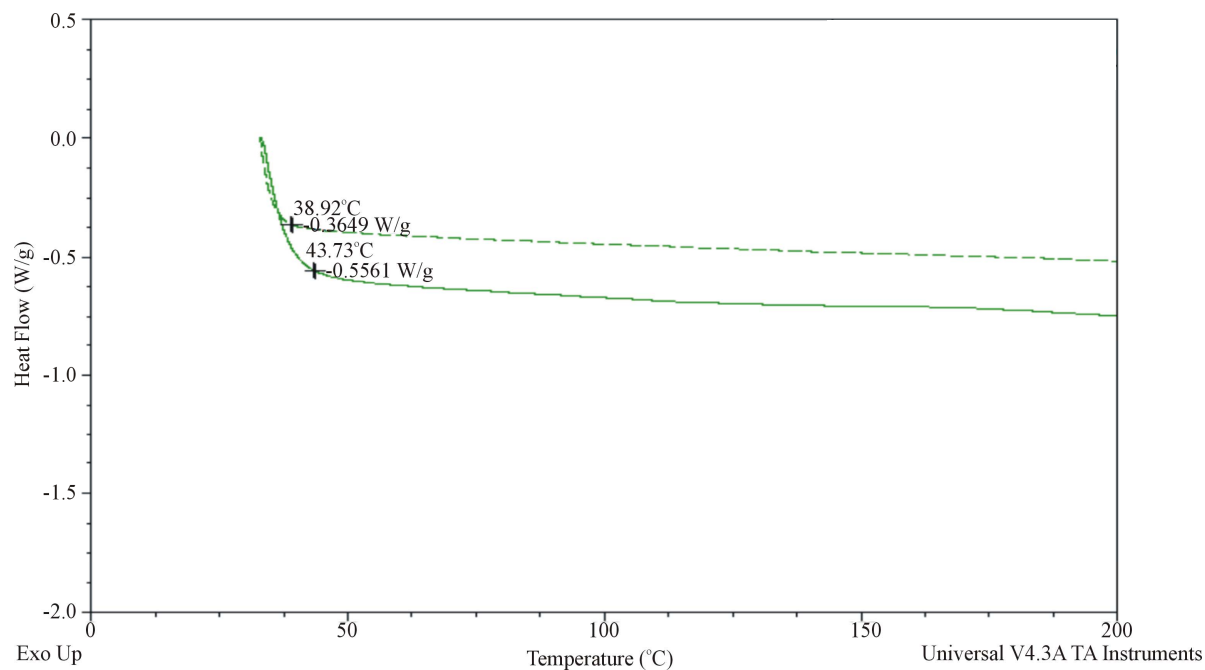
## 5. Conclusions

$\text{C}_6\text{-C}_{12}$   $\alpha$ -olefins oligomerization in the presence of chloroaluminate ionic liquids and their combination with Ti-containing complexes used as modifiers have been studied. The structure, molecular-weight characteristics and low-temperature properties of produced oligomers have been examined by means of IR, PMR spectroscopy, size exclusion chromatography and the DSC.

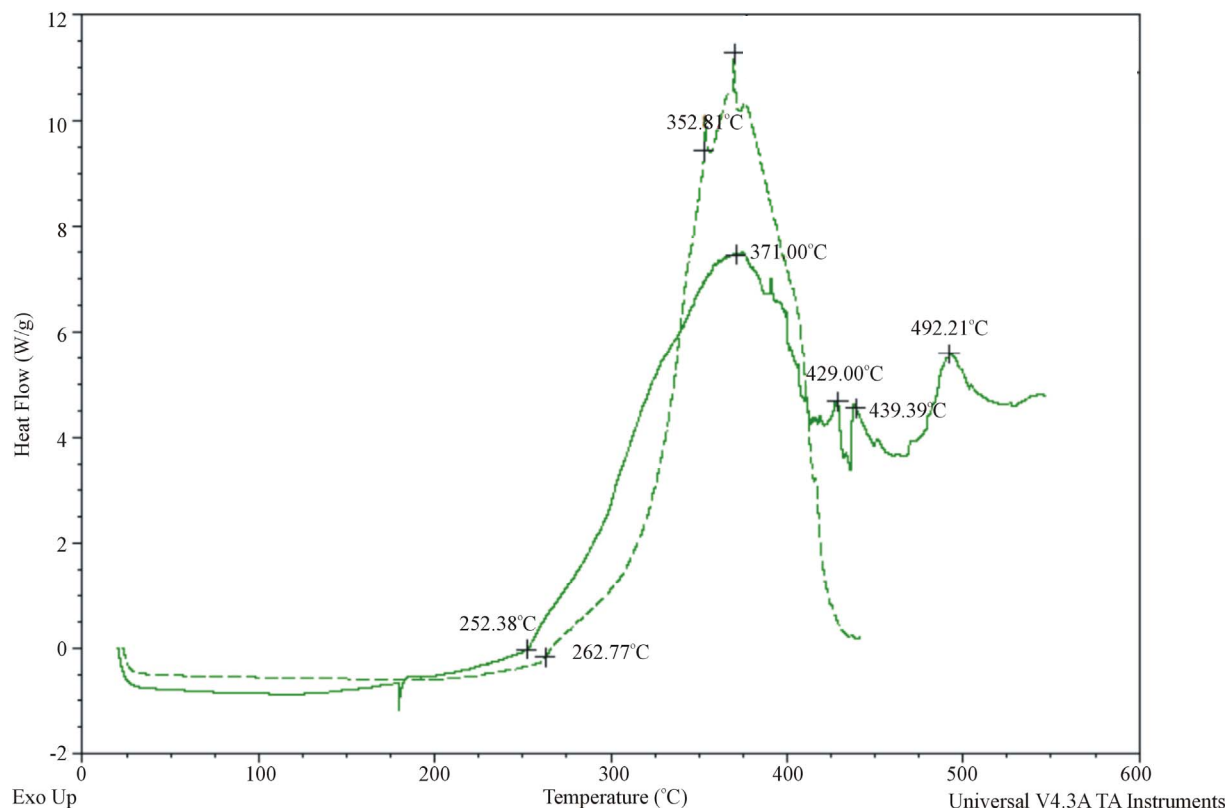
It was shown that in all cases of using ILCs, the obtained oligomers contain predominantly hybrid hydro-

Table 6. Physical - chemical properties of the synthesized oligoalkylnaphthenic oils.

Monomer	ILCS	Viscosity index (VI)	Temperature, $^{\circ}\text{C}$		Kinematic viscosity, $\text{mm}^2/\text{c}$ , at:		Density at $20^{\circ}\text{C}$ , $\text{kg}/\text{m}^3$	Colour on calorimeter, SNA, unit SNA
			Flash point	Freezing point	$V_{100}$	$V_{40}$		
$\text{C}_6$	I	108	220	-35	12.20	103.23	838.2	1.5
	II	116	224	-33	80.45	10.83	835.0	1.5
$\text{C}_7$	I	120	218	-33	90.0	12.0	838.0	1.5
	II	128	172	-28	218.09	26.23	870.0	1.5
$\text{C}_{10}$	I	124	174	-30	285.94	30.50	875.0	<2
	II	159	212	-38	145	19	870.0	1.5
$\text{C}_{12}$	I	162	210	-45	137.7	19.6	873.0	1.5
	II							



**Figure 4.** DSC thermo-stability curves (in nitrogen atmosphere) of oligododecenenaphtenic ODF before (---) and after (—) hydrogenation.



**Figure 5.** DSC thermo-oxidation (in oxygen atmosphere) curves of non-hydrogenated(---) and hydrogenated (—) oligododecenenaphtenic.

carbons of paraffinic-naphthenic structure with long alkyl radical branching termed as oligoalkylnaphtenic

hydrocarbons.

The synthesized oligoalkylnaphtenic oils are charac-



terized by low density values, high viscosity and viscosity index ( $\geq 108$ ), low freezing point ( $-33^{\circ}\text{C}$  -  $-45^{\circ}\text{C}$ ), high ignition temperature ( $\geq 172^{\circ}\text{C}$ ), good antioxidative stability, detergency and low volatility. They may be used as the high viscosity base oils with good thermo-oxidative stability or as a component for preparation of the synthetic and semisynthetic base oil compositions without use of additional hydrogenation step or by conducting it in a mild condition.

## REFERENCES

- [1] J. D. Holbrey and K. R. Seddon, *Clean Product and Processes*, Vol. 1, 1999, pp. 223-236.
- [2] A. H. Azizov and Z. H. Asadov, "Production and Usage of  $\alpha$ -Olefins and Advantages in the Metal-Complex Catalyzed Selective Oligomerization of Ethylene," *Processes of Petrochemistry and Oil Refining*, Vol. 1, 2003, pp. 44-67.
- [3] T. Welton, "Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis," *Chemical Reviews*, Vol. 99, No. 8, 1999, pp. 2071-2083.  
<http://dx.doi.org/10.1021/cr980032t>
- [4] A. H. Azizov, "Preparation Methods and Solvent Properties of Low Temperature Ionic Liquids," *Process of Petrochemistry and Oil Refining*, Vol. 1, No. 8, 2002, pp. 90-115.
- [5] A. H. Azizov, "Low Temperature Ionic Liquids in Organic and Petrochemical Synthesis," *Processes of Petrochemistry and Oil Refining*, Vol. 2, No. 9, 2002, pp. 6-48.
- [6] R. V. Aliyeva, "Ionic Liquids in Catalysis Petrochemical Processes," *Processes of Petrochemistry and Oil Refining*, Vol. 1, No. 16, 2004, pp. 26-46.
- [7] R. V. Aliyeva, "Ionic Liquids during Separation and Extraction," *Processes of Petrochemistry and Oil Refining*, Vol. 2, No. 25, 2006, pp. 30-39.
- [8] A. A. Xanmetov, Kh. H. Asgerova, R. V. Aliyeva and A. H. Azizov, "Ionic Liquids to Oligomerization and Polymerization Processes of Olefins," *Processes of Petrochemistry and Oil Refining*, 11, 42, 2010, pp. 309-328 (in Russian).
- [9] P. Wasserscheid, "Green Industrial Applications of Ionic Liquids," Kluwer Academic Publishers, Boston, 2003, pp. 29-47.
- [10] K. R. Seddon, "Ionic Liquids for Clean Technology," *Journal of Chemical Technology and Biotechnology*, Vol. 68, No. 4, 1997, pp. 351-356.  
[http://dx.doi.org/10.1002/\(SICI\)1097-4660\(199704\)68:4<351::AID-JCTB613>3.0.CO;2-4](http://dx.doi.org/10.1002/(SICI)1097-4660(199704)68:4<351::AID-JCTB613>3.0.CO;2-4)
- [11] H. Olivier, "Recent Developments in the Use of Non-Aqueous Ionic Liquids for Two-Phase Catalysis," *Journal of Molecular Catalysis A*, 146, 1999, pp. 285-289.
- [12] H. Olivier, J. A. Chodorge and P. Travers, "Olefin Oligomerization with Homogeneous Catalysis," *Petroleum Technology Quarter (PTQ)*, Autumn, 1999, p. 141.
- [13] A. H. Azizov, et al., "Selective Synthesis and the Mechanism of Formation of the Oligoalkylnaphthenic Oils by Oligocyclization of 1-Hexene in the Presence of Ionic-Liquid Catalysts," *Applied Catalysis A: General*, Vol. 375, 2010, pp. 70-77.
- [14] N. R. Bektashi, A. M. Mustafayev, Qusyynov, et al., "Chromatographic Investigation of Regularities of Synthesis of Halogen-Containing Unsaturated Polyesters," *Journal Prikladnoy Khimii*, Vol. 84, No. 7, 2011, pp. 1211-1217 (in Russian).
- [15] K. Nakanisi, "Infra-Red Spectra of Complex Molecules," Publishing House of Foreign Literature, Moscow City, 1963, p. 25 (in Russian).
- [16] L. Bellami, "The Infra-Red Spectra of Complex Molecules," Publishing House of Foreign Literature, Moscow City, 1963, p. 25 (in Russian).
- [17] E. Breitmayer, "Carbon-13 NMR Spectroscopy," 3rd Edition, VCH, Weinheim, pp. 183-196.
- [18] "Nefteprodukti Metodi Ispitaniy Part 1, Izdatelstvo Standartovç Moskva," 1977 (in Russian).
- [19] B. V. Belyanin and V. N. Erikh, "Tekhniçeskiy Analiz Nefteproduktov i Qaza," Leninqrاد, Chimiya, 1979, pp. 111-112 (in Russian).