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Oligomerization and alkylation decene-1 in the presense chloroaluminate ionic liquids

Akif Hamid Azizov[1], **Reyhan Valy Aliyeva**[1],
Khayala Haydar Seidova[1], **Esmira Mustafa Karayeva**[1],
Igrar Geyrat Nazarov[2], **Aygun Muzaffar Abdullayeva**[2]

[1]The Institute of Petrochemical Processes named after acad. Y.H. Mammedaliyev of Azerbaijan National Academy of Sciences, Azerbaijan, Baku
[2]Baku branch of Moscow State University after M. V. Lomonosov, Azerbaijan, Baku

Email address

xayala_550@rambler.ru (K. H. Seidova), akazizov@ymail.com (A. Azizov), alreyhan@yahoo.com (R. Aliyeva), niqrar@gmail.com (I. G. Nazarov), 89abdullayeva@mail.ru (A. Muzaffar)

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Abstract

In this present paper, the results oligomerizaton and alkylation of decene-1 in the presence of recyclable chloroaluminate type ionic-liquid catalysts. The composition and structure of oligoalkyl (naphtenic) products obtained in the presence of ionic-liquid catalysts studied by different methods of analysis. The oligomerization of decene-1 in various conditions in the presence of the ionic liquid of chloroaluminate type has been carried out, the kinetic curves have been constructed.

1. Introduction

Technological advances are often accompanied by a variety of unanticipated problems and complications. Advances in the function and efficient operation of modern machines and engines have brought new challenges relating to the satisfactory use and performance of existing oils. PAO are gaining rapid acceptance as high performance lubricants and functional fluids because they exhibit certain inherent and highly desirable characteristics. Products oligomerization and alkylation of alpha olefins are a class of synthetic high performance functional fluids that have been developed to meet the increasingly stringent demands being placed on today's working fluids. In recent years, many papers published for using ionic liquid catalyst systems (ILCS) for the α-olefins oligomerization and alkylation processes. Development research in the field the oligomerization of α-olefins in the presence of ILCS sometimes is difficult due to absence of information on the kinetic parameters of the process, as well as a detailed understanding the formation mechanism of the macromolecules during oligomerization processes [1-6].

The result of the researches are included in this paper on oligomerization of decene-1 and alkylation her with toluene in the use of chloroaluminate ionic-liquid type catalytic systems and determination of structural, molecular weight, viscosity and other physicochemical characteristics of the synthesized oligomer samples and establishment some kinetic parameters of the process.

2. Experimental

All the works on synthesis of the components and ILCS and also on carrying out of decene-1 oligomerization and alkylation process her with toluene were carried out in an inert atmosphere with use of starting reagents purified by distillation or recrystallization before experiments.

The following reactants are used in the work:

a) decene-1 ($C_{10}H_{20}$) (Alfa Aesar/A Johnson Matthey Company (Germany)) – colorless liquid with specific pungent smell; molecular weight -140,27 g/mol; boiling point ($T_{boil.}$=166,5-173,5^{0}C; density (d)=0,741 g/ml, n_d^{20}=1,421;

b) aluminum chloride ($AlCl_3$): colorless trigonal crystals: molecular weight 133,5 g/mol; distillation temperature (T_{dis}) =180^{0}C;

c) triethylamine hydrochloride ($C_6H_{15}NCl$) (Alfa Aesar/A Johnson Matthey Company (Germany)); molecular weight 138,5 g/mol;

d) diethylamine hidrocloride ($C_4H_{12}NCl$) *(Alfa Aesar, Johnson Malthey Company*(Germany)), molecular weight 109,5 g/mol; T_{melt} = 220 °C; Tboil = 330 °C; d = 1,041 g/sm^3 (21°C) ;

e) toluene (C_6H_5-CH_3). (Cherkasky plant chemical reagents) Colorless volatile liquid with a pungent odor, soluble in most organic solvents T_{melt}:-94,9°C, T_{boil}:110,6°C; molecular weight 92,14 g/mol. d^{20}=0,86694 g/sm^3;

f) $[EMİM]^+$ $[HSO_4]^-$ (*Alfa Aesar, Johnson Malthey Company,* (Germany)), Brutto form: $C_6H_{12}N_2O_4S$; molecular weight 240 g/mol;

$[BMİM]^+$ $[BF_4]^-$ (*Alfa Aesar, Johnson Malthey Company,* (Germany)), Brutto form: $C_8H_{15}BF_4N_2$; molecular weight 226 g/mol.

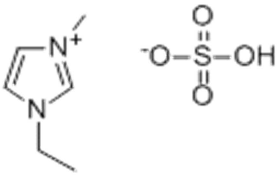
Chloroaluminate ionic – liquids were prepared by interacting $AlCl_3$ with the corresponding complex ammonium salt taken at molar ratios 1÷ 2:1. Synthesis of the ionic-liquid catalytic systems and also oligomerization decene-1 and alkylation with toluene of in their presence were carried out in the thermostarted dried up glass reactor in the atmosphere of dry nitrogen or argon.

Synthesis of ILCS and also oligomerization decene-1 and alkylation her with toluene of in their presence were carried out in the thermostarted dried up glass reactor in the atmosphere of dry nitrogen. 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 $AlCl_3$ was added to the obtained complexes at intensive mixing in a nitrogen current. Catalyst preparation was accomplished at 20°C - 25°S during 10 min. The ILCS obtained represented themselves as the yellowish viscous liquids at room temperature. By this method the following ILCS were prepared to be used as a catalyst in the decene-1 oligomerization and alkylation her with toluene:

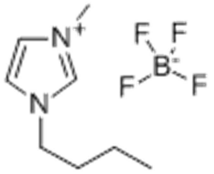
$[(C_2H_5)_2NH_2]^+[Al_2Cl_7]^-$ ILCS I

$[(C_2H_5)_3NH]^+[Al_2Cl_7]^-$ ILCS II

For environments catalytic systems used ionic liquid (IM):



$[EMİM]^+$ $[HSO_4]^-$ (IM I)



$[BMİM]^+$ $[BF_4]^-$ (IM II)

Upon termination of synthesis of the chloroaluminate ILCS decene-1 was introduced into reactor though a drop funnel at intensive mixing. Experiments on oligomerization were carried out at temperature 30-100^{0}C during 0.3-3 hours also at intensive mixing.

Chloroaluminate ionic liquid prepared as described above, then in reactor under nitrogen atmosphere, was added reactant toluene and addition funnel decene-1. The test was conducted for 3 hours at a temperature 95-100^{0}C under constant mixing with a stirrer.

After the termination of oligomerization and alkylation reaction the obtained product were separated from catalyst remaining by washing off them with 10% solution of the sodium hydrate, and were dried up over calcinated Al_2O_3. 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.

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 100A° were used. Dimethylformamide was used as an eluent (flow rate 0.3 ml/min, temperature 20-25 ^{0}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 (Fig. 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. Average molecular weights (Mw and Mn) were calculated using the following formulas:

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

where M_i is the molecular weight, corresponding to the i^{th} slice of the chromatogram; ω_i is the area fraction of the i^{th} slice.

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 ºC/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 sm^{-1} .

PMR spectra were recorded on a Brunker 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. Results and Discussion

In table 1 shows the conditions of oligomerization of decene-1 and alkylation with toluene in the presence IMKS and yield of the products.

Table 1. *Conditions of the oligomerization of decene-1 and alkylation with toluene in the presence IMKS*

№	Component	AlCl$_3$, %	Catalytic systems, molar ratio	IM	T, ° C	Fractions (^{0}C), %			Fraction (>200^{0}C) mass. %
						I (65-115)	II (120-175)	III (>200)	
1	C_{10}+tolyene	3	AlCl$_3$	-	60	30	3.3	62	42,4
2	C_{10}+tolyene	6	AlCl$_3$	-	60	1,1	17.5	78	44.9
3	C_{10}	6	AlCl$_3$: TryEtAHCl 1.7 : 1	-	60	-	-	88,6	85
4	C_{10}	6	AlCl$_3$: DyEtAHCl 1.7 : 1	-	60	-	-	75	72
5	C_{10}+tolyene	6	AlCl$_3$: DyEtAHCl 1.7 : 1	-	95-100	8.4	38.2	52.13	48
6	C_{10}+tolyene	3	AlCl$_3$: ТЭАГХ 1.5 : 1	I	95-100	52.0	32.42	14.7	13.1
7	C_{10}+tolyene	6	AlCl$_3$: ТЭАГХ 1.7 : 1	II	95-100	13.3	60.3	25.4	23.4

4.1. Molecular Weight Characteristics of the Products

MWD parameters of some samples of decene-1 oligomerization and alkylation product obtained in the presence of various ILCS are given in figure-1 and in table 2.

a) oligomerization products

b) alkylation products

Fig. 1. *MWD curves of the decene-1 oligomerization and alkylation (with toluene) products obtained in the presence various ILCS*

As is seen from tab. 1, the oligomerization products of decene-1 received in the presence of ILCS-I and ILCS- II have the MM indexes within the limits- M_w=4450-5180, M_n=3740-4540, where MMD coefficient changes within M_w/M_n = 1,14-1.19. Anyway in each system the received MMD indexes change in the narrow limits.

But the alkylation products of decene-1 by toluene received in the presence of ILCS-I and ILCS- II have the MM indexes within the limits- M_w=534-950, M_n=434-730, where MMD coefficient changes within M_w/M_n = 1,23-1.3.

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

№	Components	ILCS	M_w	M_n	M_w/M_n
1	C_{10}	I	4450	3740	1.19
2	C_{10}	II	5180	4540	1.14
3	C_{10}+tolyene	I	534	434	1.23
4	C_{10}+tolyene	II	950	730	1.3

4.2. The Structure Oligomerization and Alkylation Products

The structures of the oligomers obtained were explored by IR-and PMR-spectroscopic methods and DSC analysis.

IR spectrum of decene-1 oligomers (figure 2), synthesized at the presence of chloroaluminate ILCS are characterized by presence of absorption bands related to the long chained alkyl groups: 720 sm^{-1}-deformation pendular fluctuations of CH_2 groups in the (-CH_2-)n sequence, 1380 sm^{-1} –symmetric deformation fluctuations of CH_3 groups. The intensive absorption band at 1460 sm^{-1}¬ is caused by the imposing fluctuations of CH_3- groups and asymmetric deformation fluctuation of CH_2 groups. In the spectra of the investigated decene-1 oligomers the absorption bands of vinyl (910 and 1640 sm^{-1}) and trans vinylen (970 sm^{-1}) double bonds practically do not contain. Nevertheless in the fields of 890 sm^{-1} very weak absorption related to vinyliden double bonds may be are observed. In the spectra there are absorption bands at 980 sm^{-1} 1020 sm^{-1} characteristic to oscillatory movements of a carbon skeleton of the naphthenic rings, and at 900 sm^{-1}, responsible for the hydrogen atom of the isolated naphthenic cycles.

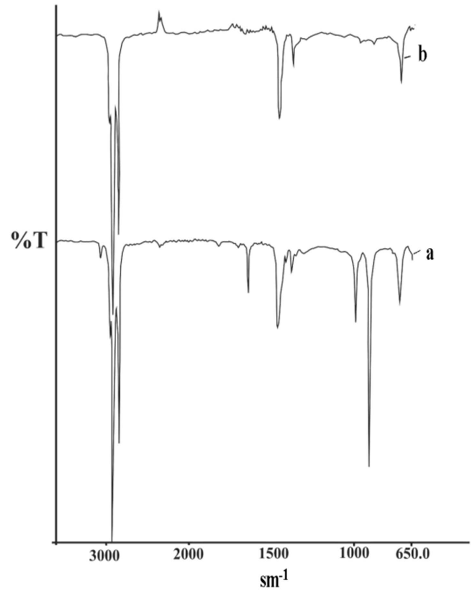
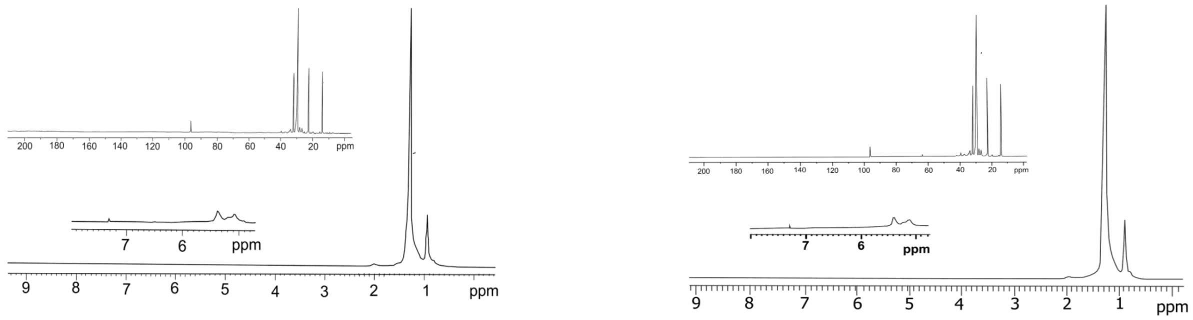


Fig. 2. *IR spectrum of decene-1 (a)and of oliqodecene fraction (b) , produced in the presence of ILCS-I.*

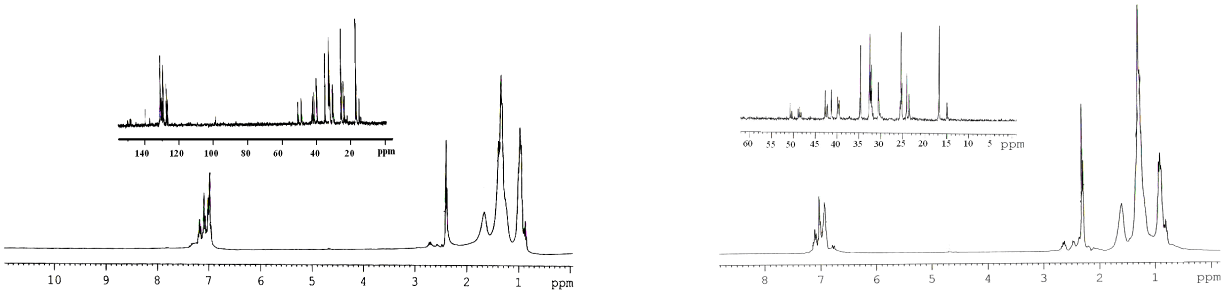
Insignificant content of saturated bonds in the structures of the oligomerization products is confirmed also by values of iodine numbers of products (0,042-0,75 mg J_2/100 g a product), that is much less than it may be expected from theoretical considerations.

The results of definition of the structural parameters of the synthesized oligomers by PMR-spectroscopy method are consistent with the data of IR spectral analysis. In particular, in PMR- and ^{13}C NMR spectra of all the synthesized oligodecene samples (figure 3) are contained the signals of resonance absorption of the protons of methyl (0,98 ppm) and methylene (1,28-1,3 ppm) protons, together with the bands of the weak resonance absorption in the field of 1,5-1,8 ppm, corresponding to the chemical shifts of the protons in the naphthenic structures.

At considerable enhancing of absorption resonance signals by accumulation in the PMR spectra of oligododecene appear the weak signals from the protons of methylene groups (5.0-5.5 ppm) in CH=CH$_2$, and also vinylene groups CH=CH (5.7 ppm).



oligomerization decene-1 in the presence ILCS



alkylation decene-1 with tolyene in the presence ILCS

Fig. 3. *^{13}C NMR and PMR spectra of oligodecene fraction produced in the presence ILCS*

It means, that the most part of the oligomer molecules which have stopped their growth in the course of decene-1 oligomerization, does not contain any double bonds or their considerable share have a structure of the type $R_1R_2C=CR_3R_4$. which does not show signals in PMR spectrum. However, presence in PMR spectra, and ^{13}C spectra of the signals from napthenic structures testify to the oligoalkylnaphtenic nature of the most part of oligodecene molecules.

It is interesting to notice, that in ^{13}C NMR spectra are present signals not only from five- and six- numbered naphtenic rings, but also from seven-numbered rings. This fact indirectly indicates to the predominat proceeding of the cyclization reaction in the last unit of the growing oligomer chains.

The results of IR-, PMR and NMR spectral analyses have shown identity of frames of all investigated oligodecene 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.

Results structure determination synthesized oligoalkylation fraction (OAF) (> 250°C) by PMR- and ^{13}C NMR spectroscopy have confirmed these IR spectral analysis. In particular, PMR- and 13C NMR spectra of synthesized samples OAF contains the resonant absorption band of the methyl protons (0.98 ppm), methylene (1.28 - 1.3 ppm) corresponding to the chemical shift of the protons in the alkyl group. With a significant enhancement of resonance absorption by the accumulation in the PMR spectra appear weak bands of protons of the methylene groups (5.0 - 5.5 ppm) with CH = CH2, and vinylene (5.7 - 5.7 ppm) CH = CH groups, indicating that a small amount of double bonds in the composition of the products obtained. In each case, multiplet signals observed in the region 6.8 - 7.9 ppm corresponding substituted aromatic rings.

Thus, the characteristic absorption band IR (781, 814, 1511, 1604, 3017 sm^{-1}) signals by NMR (1H, 13C) (6,8-7,9 ppm) indicate the presence of (oligo)alkylaromatic compounds in the heavy fraction (> 200 ° C).

5. Some Physical and Chemical Properties Oligomerization and Alkylation Products

Some physicochemical indexes of oligomerization and alkylation products, produced in the presence of ILCS-I and ILCS-II, have also been estimated. The results are presented in Table 3. The values of viscosity index (VI) have been calculated in accordance with GOST 25371-97.

Table 3. *Some physical-chemical indexes of oligodecene fractions received in the presence of ILCS*

№	**Component**	**ILCS**	**IV**	**Kinematic viscosity, mm^2/s**		**Density 20^0C, kg/m^3**	**n_d^{20}**
				V_{100}	**V_{40}**		
1	C_{10} +tolyene	II	88	1.79	5.61	0.8387	1.3030
2	C_{10} +tolyene	I	105	1.67	4.95	0.8433	1.4747
3	C_{10}	I	128	26.23	218.09	0,8410	-

On the DSC of the firm Thermelectron Corporation USA with heating rate 10 degree/min there have been carried out in air or nitrogen atmospheres the thermal analysis of the obtained decene-1 oligomerization and alkylation product. DSC study the OAF (> 200° C) indicate that product obtained in the presence ILCS of a thermostable on average up to 190 -200°C. DSC study the oligomerization product (> 350 °C) indicate that product obtained in the presence ILCS of a thermostable on average up to 252 °C.

6. Kinetic Reguliarities of Oligomerization of Decene-1 in the Presence of the ILCS

For establishment of primary kinetic regularities of process the reactions were carried out in three various directions: a) at various temperatures: 30^0C, 60^0C, 80^0C, 100^0C (in this the constants are 2,3% ILCS II and $AlCl_3$: TryEtAHCl =1-1,7:1 mol); b) at various ratios of components $AlCl_3$: TryEtAHCl =1-2:1 (in this constant are quantities of ILCS II 3% and temperature 60^0C); c) in various quantities of ILCS II -1÷6% (in this constant are temperature 60^0C and ratios of components $AlCl_3$: TryEtAHCl =1,3:1). An analysis of the kinetic curves prepared in various conditions shows a strong dependence of their form on various factors, in particular on conditions of carrying out of reactions. In spite of general similarity of curves they are differed from each other. As it is seen at 30^0C temperature it is more clearly fixed an induction period and in the range of 10-40 min. has a straight-line form. At temperature rise from 60 to 100^0C an induction period is not visually observed and in this case the preparing catalytic centers are characterized by high activity (first 15 min. a yield of oligomer is high and is higher 75%). At 100^0C a conversion of decene-1 practically reaches ~99%. In general, with temperature rise the form of kinetic curves passes from S-figurative to sloping. S-figurative form of the kinetic curves has been connected with simultaneous formation and deactivation of the active centers. A deactivation of the active centers leads to the decrease of yield of oligomer preparing at temperature 30^0C. In deactivation of the active centers a flocculation of ILCS is observed and as a result a “death” of the active centers occurs gradually. At low temperature (30^0C) the reaction order is close to zero where it is changed a character of total equation describing a process. A reason of this can be the most heterogeneous nature of catalyst.

On the basis of logarithmic values the semi logarithmic anamorphoses in kinetic curves fixed at various temperatures (in this the constants are 2,3% ILCS and $AlCl_3$:TEAHC=1-1,7:1 mol) have been constructed (fig. 4).

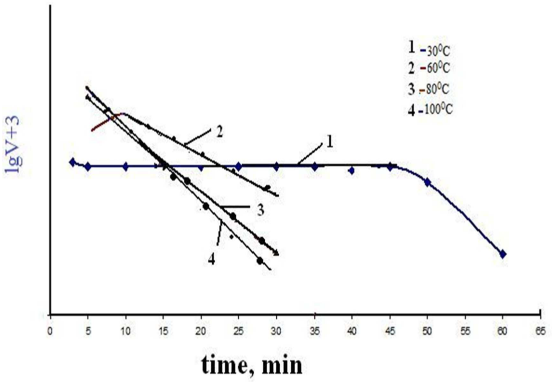


Fig 4. *Semi logarithmic anamorphoses in kinetic curves at various temperatures (AlCl$_3$: TryEtAHCl =1,7:1; total content of ILCS-2,3 %; temperature, ^{0}C: 1-30 ±5, 2-60±5, 3-80±5, 4-100)*

As is seen after acceleration in the initial period, a straightness of semi logarithmic anamorphoses in the definite range confirms a quasi-stationary stability of centers forming in the system. At low temperatures (30^{0}C) the reaction order rate is close to zero and reaction rate in time dependence graphics is changed in parallel to axis. As the reaction order is less 1 (close to zero) a character of total equation is changed. This is explained by the most heterogeneous nature of catalyst. At high temperatures ILCS plays a role of solvent and monomer is well dissolved in it. At low temperature ILCS is subjected to the flocculation and therefore the catalyst passes from homogeneous state to heterogeneous state. As a result a medium becomes less dispersed. In this case the reaction from kinetic field passes to diffusion one. This factor can also become a reason of decrease of reaction rate. Usually in diffusion region the reaction rate is small and cloddy-formation factually leads to the deactivation of the catalyst. At first after increase of the reaction rate a disturbance of straightness of semi logarithmic anamorphose shows a deactivation of the active centers or conversion of highly reactive active centers into less weak ones (fig.4). At oligomerization of decene-1 at 30^{0}C temperature in the presence of ILCS for first 5 min the oligomerization rate grows and for 5-45 min. is not changed, i.e. in this range the oligomerization rate doesn't depend on time. With time the process rate falls essentially. This evidences about extreme character of dependence of deactivation of the active catalytic centers (and also can be as a result of change of viscosity of process).

On the basis of graphically calculated data of the corresponding quasi-stationary part of the kinetic curves a dependence of lgV-10^3/T is constructed and it is calculated the activation energy which is 12 kC/mol. This number coincides with number calculated by computer program.

7. Conclusion

Carried out research decene-1 oligomerization and alkylation her with toluene in the presence IMKS indicates the efficiency of the processes. Yields of the products identified and studied in their structure.

It was shown that in all cases of using ILCs, the obtained oligomer product contain predominantly hybrid hydroterized by low density values, high viscosity and viscosity index (≥128), low freezing point (−33°C - −45°C), high ignition temperature (≥172°C), good antioxidative stability, detergency and low volatility. They may be used as the high viscosity base oils with good thermooxidative 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. Spectroscopic analyzes in the alkylaromatic fractions indicate the presence of (oligo)alkylaromatic compounds in the heavy fraction (> 200 ° C). These products are thermally stable at an average of 190-200 ° C.

Thus, decene-1 oligomerization process carried out in the presence of chloraluminate type catalytic systems in various conditions and on the basis of the constructed kinetic curves and mathematical calculation it has been established that the character of curves is changed with temperature, at high temperature (60-100^{0}C) the oligomerization process on monomers – on first and on catalyst – on second order.

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