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Investigation of interaction of nitrils with aliminium/organic compositions

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Abstract
Complex formation is widely used as a method of directed change of rate and selectivity of polymerization processes and structure of the obtained polymer. Introduction of complex formation can cause significant influence on reaction ability of monomers. The given work concerns the study of complex formation of Et_2 *AlCl* with nitrils. Nitrils CH_2 = *CHCN* and others have two reaction centers, capable to complex formation with t_2*AlCl* : *CN* group and *C=C* contact.

Keywords: acetonitril *(AN)*, acrylonitril *(ACN)*, monomer, benzol, heptane

Introduction
It has been shown in a number of works that when heteroatom *S* or *O* capable to donor – acceptor interaction is connected directly to sp^2 – carbon atom, its complex formation ability has been suppressed. If sp^2 – carbon atom is in β position related to heteroatom, complex formation ability of the latter is partially restored. Availability of double connection conjugate to *C* ≡ *N*, increases donor properties of the latter. At the expense of polarization of π- electrones of more electronegative atom of nitrogen, aluminum atom rather easily forms complexes with electrones donors [1].

Experiment
For analysis of interaction of acetonitril (*AN*) and acrylonitril (*ACN*) with Et_2 *AlCl* in benzol, heptane CCl_4 *IR* spectrophotometr *IR-20* was used in 650-1900 sm^{-1} area. The researches were carried out in liquid dish with windows from *NaCl* and *KBr* in argon atmosphere. The thickness of the later for all measurements is *0.11mm*. Spectrums of PMR were taken in spectrometer. "Variant-60" is in brazed ampoules. Et_2AlCl with the following characteristics were used: C_{Al} = *69.77%* in gasoline, $d=0.865g/sm^3$, *Cl/Al=1.25*, C_{Al}=*63.38%* in gasoline, $d=0.870g/sm^3$, *Cl/Al=1.25*.

Discussion of the Results
İnteraction nitrils with Et_2AlCl was studied in 0.5-1.6:1 mole/mole correlation. Distribution of electron density on atoms *C* and *N* ground to suppose that complex formation proceeds on *CN* group. Analysis of *IR* spectors proves this assumption as shift of valent vibration *C≡N, AN* and *A* stripes takes place from 2240 sm^{-1} in 70-80 sm^{-1} into long wave area. Analysis of the process kinetics showed that complex formation Et_2 *AlCl-AN* or *AKN* is a balanced process and whole disappearance of free groups *C≡N* (according to *IR*-spectroscopy) is observed in correlation of Et_2 *AlCl*:*N*=1.5 (*in* C_6H_6), 1.3(*in* CCl_4), but in heptane balanced concentration Et_2 *AlCl* remains enough high in any correlation of components. Values of constant of complex formation reaction balance are shown in table1.

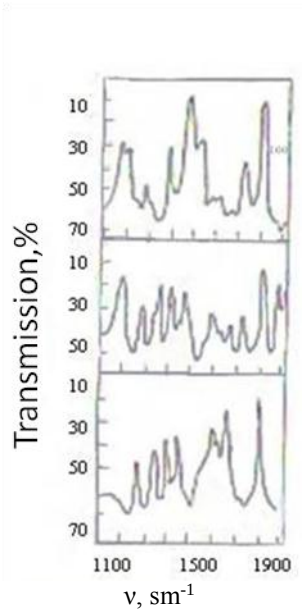

Fig 1: *IR* –spectrs of *AN* and its complexes with Et_2 *AlCl* in benzol
a) AN,
b) Et_2 *AlCl*:*AN* = 0.5
c) the same correlation 1.5

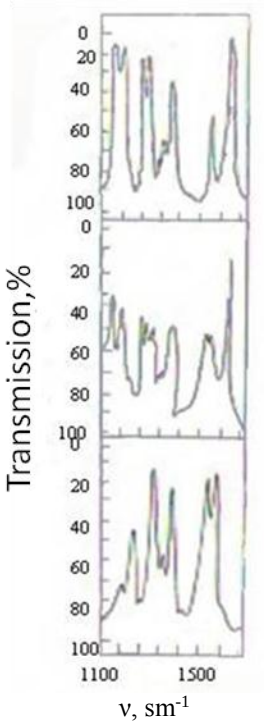

Fig 2: *IR* –spectrs of *AN* and its complexes with Et_2 *AlCl* in benzol
a) AKN,
b) Et_2 *AlCl*:*AKN* = 0.5
c) the same correlation 1.5

Table 1: Constants of complex formation balance *AN* with Et_2 *AlCl* in various solutions.

Correlation of Et_2 *AlCl* :*AN* (mole/mole)	Kp l/mole	Solution
0.5	35.8	C_6H_6
1.0	27.3	C_6H_6
0.5	3.81	$n-C_7H_{16n}$
1.0	5.92	$n-C_7H_{16n}$
0.5	21.0	CCl_4
1.0	30.8	CCl_4

Kinetic curves of complex accumulation on time have been shown in fig 3.

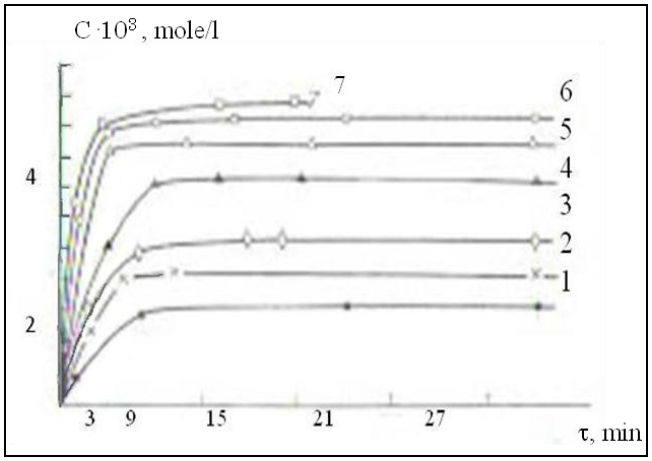

Fig 3: Dependence of the change of complex concentration Et_2 *AlCl*:*AN* (mole) – on time in benzol at 1-0.5; 2-1; 3-1.5; 4-1.55; 5-1.6; 6-1.7; 7-1.8.

While mixing of solutions *AN* and Et_2 *AlCl* intensity of the stripe *vCN* decreses and correspondingly increase of complex band intensity takes place in correlation intervals Et_2 *AlCl*:*AN* = 0.5-0.6; in correlation 1.4-1.6 regeneration of *AN* is observed, *vC≡N* band intensity increases and intensity of complex-connected cyan group band increases (fig.4). It teshfies small stability of Et_2 *AlCl*:*AN* complex in heptane.
It can be supposed recomplexing proceeds very slowly.

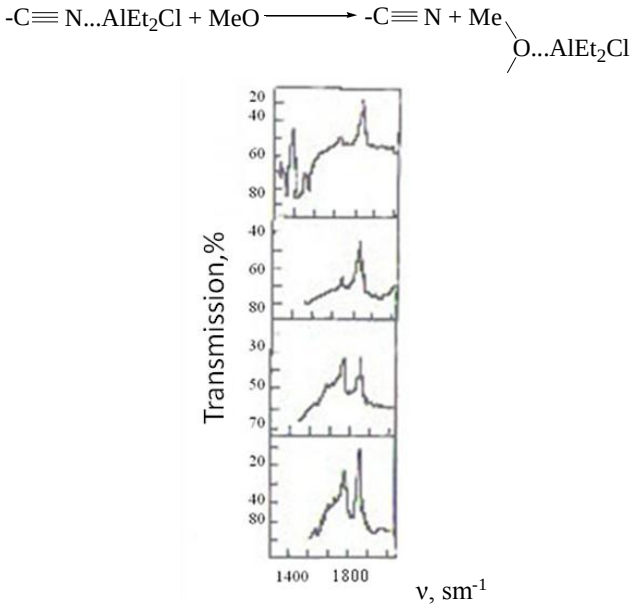

Fig 4: *IR* spectrums of *AN* and its complexes with Et_2 *AlCl* in heptane

a) (*AN*,*b*) Et_2 *AlCl*:*AN* = 0.5 in the same correlation 1.5.
Thus in interaction of nitrils with Et_2 *AlCl* complexes of *C≡N….M*, type resistant till 70℃ are formed. While formation of complexes *AN*: Et_2 *AlCl*, *AKN*:Et_2 *AlCl* displacement of (*vCN*) apprexamat on 80 sm^{-1}, long wave area approves that main center of coordination is the cyan group. Bands *vC=C* in spectrums *AN*:Et_2 *AlCl* in any correlations of the components practically do change. In *IR* spectrums *AKN*:Et_2 *AlCl* it is impossible to follow changes *vC=C*, as this area is covered with complex-connected *C≡N* band.
In order to explain the role of *C=C* connection in nitril molecule conjugated to *C≡N* group, PMR- spectrockopy method has been used in complex formation *AN* with Et_2 *AlCl* in CCl_4 [2].
PMR spectrums of mixtures solutions *AN* and Et_2 *AlCl* in CCl_4 are compared with solution spectrums of components.
The data testify reduce of electrone density on AKN protons, especially on protons of vinyl group in simultaneous increase of electrone density on protones of methylene and methyl groups Et_2 *AlCl*. Change of multiplet view from CH_2=*CH* group protons testifies *C≡N* contact reconstruction in AKN.
PMR spectrums data show that in the complex formation process both contacts were active: electron density from AKN molecule displaces to A1 and complex of donor-acceptor type is formed.
Thus investigated monomers (acrylonitrile and acetonitrile) form stable complexes with Et_2 *AlCl* with the presence of *C≡H* contact.

References

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