

## MECHANISM OF CATALYTIC ADDITIVE CHLORINATION OF ETHYLENE TO 1,2-DICHLOROETHANE

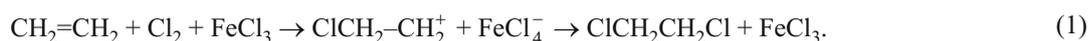
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*A mechanism for the direct additive chlorination of ethylene to 1,2-dichloroethane in the presence of FeCl<sub>3</sub> catalyst promoted by NaCl was proposed and verified. It was found that the reaction rate depends on the concentration of the active phase of the catalyst and the promoter and is also determined by their interaction with the formation of NaFeCl<sub>4</sub>. It was shown that the surface intermediate of the reaction is the Na[Fe(C<sub>2</sub>H<sub>4</sub>Cl)<sub>4</sub>] complex. A heterogeneous–homogeneous mechanism, according to which the reaction begins on the surface of the catalyst and continues in the 1,2-dichloroethane solution, was established for the process.*

**Key words:** ethylene, chlorination, catalyst, promoter, dichloroethane, mechanism, technology, conversion, selectivity, waste.

The production of 1,2-dichloroethane includes a series of stages of catalytic chlorination and oxychlorination of ethylene, which have for a number of years been the subject of investigations conducted at a series of scientific centers. In the working production of vinyl chloride in the so-called balanced scheme 1,2-dichloroethane (DCE) is produced not only by oxidative chlorination but also by direct additive chlorination of ethylene. In the direct chlorination of ethylene 1,2-DCE is obtained by the reaction of ethylene and chlorine in liquid dichloroethane under pressure of 3–4 bar at 120–125 °C in the presence of FeCl<sub>3</sub> as catalyst and NaCl as promoter according to the following scheme [1]:



Under industrial conditions FeCl<sub>3</sub> is used as catalyst and NaCl as promoter in order to increase the rate of reaction (1) and the yield and purity of the 1,2-DCE. The mechanism of the effect of the FeCl<sub>3</sub> described in the literature [2, 3] consists of electrophilic addition of chlorine to ethylene with the formation of  $\pi$  and  $\sigma$  complexes in the presence of complex structures formed during the interaction of the catalyst and the promoter. Thus, the FeCl<sub>3</sub> together with the NaCl act as carriers of the chlorine ions in its addition to the ethylene. The individual structure of these compounds was described in the monograph [4], but the nanostructured compounds that are formed during their reaction in the anhydrous 1,2-DCE medium have hardly been investigated at all [5]. Study of the mechanism of these processes is therefore important as the basis for perfecting their technology under industrial conditions, a way of reducing the material and energy expenditures, increasing their efficiency as a result of increased yield of 1,2-DCE and VC, and reducing the amount of side products (organochlorine waste products), which is extremely urgent for the organochlorine chemical industry.

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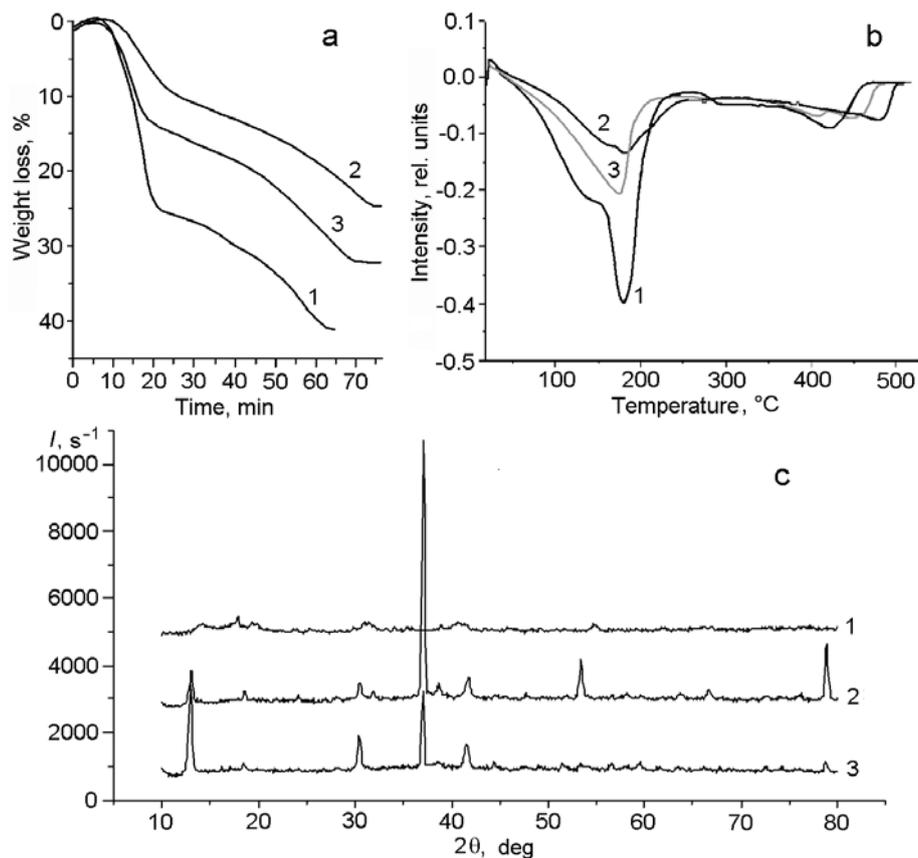


Fig. 1. TG (a) and DTG (b) diagrams of DTA analysis of samples of catalyst and the promoter for direct chlorination of ethylene, obtained from various media: 1)  $\text{FeCl}_3 + \text{NaCl} + \text{DCE}$  (solid dried precipitate from solution in 1,2-DCE (working catalyst)); 2)  $\text{FeCl}_3 + \text{NaCl} + \text{H}_2\text{O}$  (solid dried precipitate from solution in water); 3)  $\text{FeCl}_3 + \text{NaCl}$  (solid mechanical mixture,  $\text{FeCl}_3 : \text{NaCl} = 10 : 1$ ); diffractograms of samples of direct chlorination catalyst produced under various conditions (c): 1)  $\text{FeCl}_3 + \text{NaCl}$ ; 2)  $\text{FeCl}_3 + \text{NaCl} + \text{H}_2\text{O}$ ; 3)  $\text{FeCl}_3 + \text{NaCl} + \text{DCE}$ .

In this connection there is a need to elucidate the structure of the reaction sites of catalysts and to refine the chemistry and mechanism of the above-mentioned processes, which in turn will make it possible to improve the composition of the catalysts and to optimize the conditions both of their synthesis and of the regeneration that is essential under the conditions of the prolonged use of catalysts in technological processes [5].

New laboratory apparatus described in [5] was created in order to model the industrial direct chlorination of ethylene to 1,2-dichloroethane and liquid-phase chlorination at atmospheric pressure and to test new catalysts based on iron(III) chloride and sodium chloride.

Determination of the impurity content in the 1,2-DCE on a Carlo Erba GC 8000 chromatograph with a flame-ionization detector, DTA, X-ray diffraction, and mass-spectrometric analysis were used to study the structure and analyze the catalyst  $\text{FeCl}_3/\text{NaCl}$  for direct chlorination of ethylene. The investigations were conducted with three samples of the catalyst: No. 1)  $\text{FeCl}_3 + \text{NaCl}$ , a solid mechanical mixture of the crystalline forms of the components; No. 2)  $\text{FeCl}_3 + \text{NaCl} + \text{H}_2\text{O}$ , solid dried precipitate from a solution in water; No. 3)  $\text{FeCl}_3 + \text{NaCl} + \text{DCE}$ , solid dried precipitate from a solution in 1,2-DCE (the working catalyst) at the respective concentrations and  $\text{FeCl}_3 : \text{NaCl}$  ratios 100-1000 : 10-100 (ppm) [6].

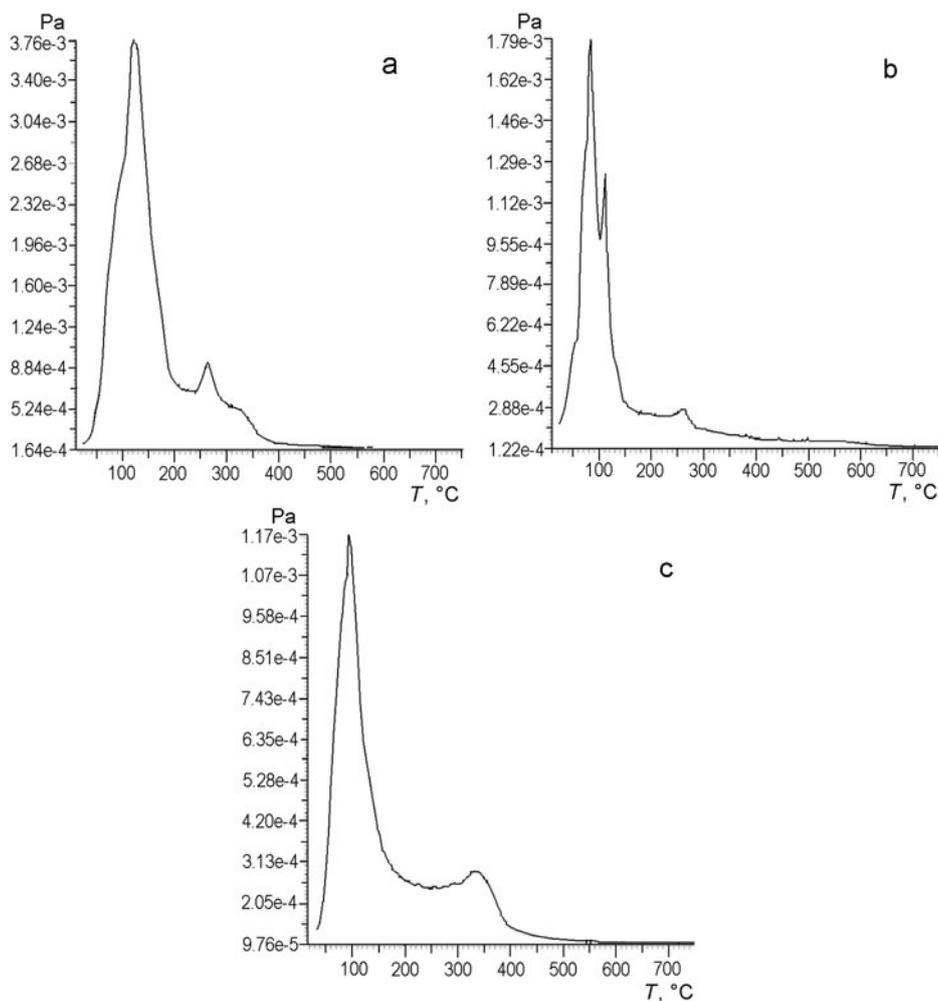


Fig. 2. Dependence of the vapor pressure on temperature during mass spectrometry for the catalyst for direct chlorination of ethylene ( $\text{NaCl}/\text{FeCl}_3$ ) in various media: a)  $\text{FeCl}_3 + \text{NaCl} + \text{H}_2\text{O}$  from aqueous solution; b)  $\text{FeCl}_3 + \text{NaCl} + \text{DCE}$  from solution of 1,2-DCE; c)  $\text{FeCl}_3 + \text{NaCl}$  mechanical mixture.

The TG and DTG diagrams of the samples are presented in Fig. 1a, b. It is seen from the TG diagram (Fig. 1a) that in the range of working temperatures for direct chlorination of ethylene (reaction (1)) **from 353 K (89 °C) to 473 K (200 °C)** the mechanical mixture No. 1 and the mixture obtained by evaporation from aqueous solution No. 2, where they do not form any intermediate compounds under normal conditions, have the smallest weight losses (8%-12%).

At the same time, for mixture No. 3 ( $\text{FeCl}_3 + \text{NaCl} + \text{DCE}$  (working catalyst)) the weight losses during heating is two or more times higher (24%). More detailed analysis of the DTG curves in Fig. 1b shows that only sample No. 3 ( $\text{FeCl}_3 + \text{NaCl} + \text{DCE}$ ) has two maxima for the dissociation rate of two intermediate compounds at 125 and 180 °C, whereas the mechanical mixture No. 1 and the mixture from the aqueous solution No. 2 have only one maximum for the dissociation of one compound in the region of 180 °C. It is consequently possible to speak of the presence in the composition of the working catalyst ( $\text{FeCl}_3 + \text{NaCl} + \text{DCE}$ ) of two intermediate compounds, for which in total the losses increase to 24%, while the total losses for DTA of this sample are significantly higher and amount to 42% in contrast to the sample of the mechanical mixture (33%) and the mixture obtained after drying of the aqueous solution ( $\text{FeCl}_3 + \text{NaCl} + \text{H}_2\text{O}$ ) with 24% (Fig. 1). Then, during X-ray diffraction (Fig. 1c) it was shown that a new poorly crystalline  $\text{FeCl}_n$  phase at  $2\theta$  in the region of  $12.5^\circ$  was detected in the diffractogram of

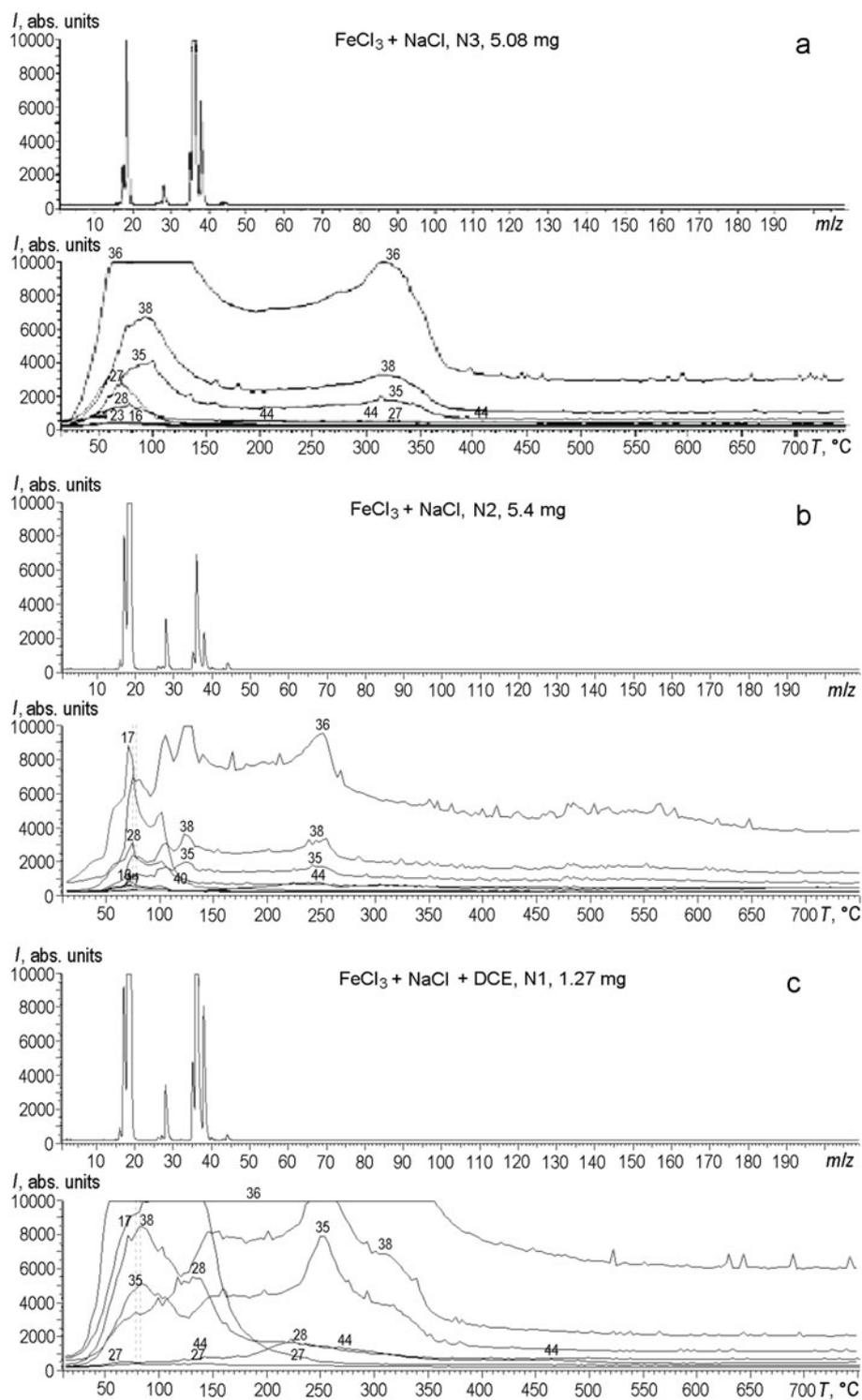


Fig. 3. Thermal desorption mass spectroscopic curves for decomposition of the active phase of the catalyst for direct chlorination of ethylene: a) NaCl + FeCl<sub>3</sub> (mechanical mixture;  $t = 76.0$  °C); b) NaCl + FeCl<sub>3</sub> + H<sub>2</sub>O (after drying from aqueous solution;  $t = 74.8$  °C); c) NaCl + FeCl<sub>3</sub> + DCE (after drying from solution in DCE;  $t = 78.6$  °C).

TABLE 1. Results of Investigation of the Stage of Direct Chlorination of Ethylene to 1,2-DCE under Industrial Conditions

Expt. No.	Composition of catalyst		Quantitative composition of products of direct chlorination of ethylene to 1,2-DCE according to chromatographic analysis							
	FeCl <sub>3</sub> , ppm	NaCl, ppm	C <sub>2</sub> H <sub>4</sub> , %	VC, %	CTC, %	CHCl <sub>3</sub> , %	TCEt, %	DCE, %	TCE, %	TetCEt, %
1	1622	53.4	0.002	0.005	0.05	0.062	0.003	99.28	0.493	0.0033
2	1843	50.8	0.239	0.07	0.041	0.048	0.003	98.83	0.707	0.015
3	1325	58.8	0.010	0.007	0.07	0.095	0.003	99.08	0.636	0.05
4	1532	53.4	0.002	0.001	0.011	0.013	–	99.13	0.793	0.002
5	1766	51.3	0.155	0.066	0.02	0.021	–	99.13	0.506	0.006
6	1718	50.8	0.007	0.024	0.057	0.063	–	98.97	0.516	0.009
7	1785	51.3	0.176	0.003	0.022	0.026	–	99.44	0.239	0.006
8	1645	50.8	0.1	0.011	0.01	0.013	–	99.40	0.397	0.002
Average	1522	51.4	0.1	0.024	0.032	0.052	0.003	99.13	0.54	0.013

sample No. 3 (FeCl<sub>3</sub> + NaCl + DCE) obtained on the DRON-UM1 diffractometer in CoK radiation with a Fe filter in reflected beams.

The ratio of NaCl and FeCl<sub>3</sub> in samples Nos. 2 and 3 was different. Whereas NaCl predominates in sample No. 2, the FeCl<sub>n</sub> predominates in sample No. 3. It is thus possible to confirm the previous suggestion about the formation of two intermediate compounds between NaCl and FeCl<sub>n</sub> from the solution in 1,2-DCE in sample No. 3. This was also noted during DTA analysis. It is also possible to speak of polyvalence in the iron chlorides (Fe<sup>+2,3,n</sup>) in the compounds of FeCl<sub>n</sub> with NaCl, which envisages the creation of complex compounds of the Na(FeCl<sub>n</sub>) type where  $n = 1, 2, 3, 4$ .

Additionally, a mass spectroscopic investigation of all the above-mentioned samples was undertaken in order to determine the structure of the compounds of the catalyst and the promoter Na(FeCl<sub>n</sub>) produced in the various media. A complex temperature dependence of the vapor pressure was established during thermal desorption mass spectroscopy for the catalyst of direct chlorination of ethylene (NaCl/FeCl<sub>3</sub>) synthesized in various mediums (Fig. 2a-c). Unlike the mechanical mixture and the mixture produced from an aqueous solution, for the catalyst and promoter prepared from a solution of 1,2-DCE there are two desorption peaks at 353 K (80 °C) and 393 K (120 °C), which confirms the complex structure of this complex compound.

Figure 3a-c presents the results from thermal desorption analysis of the active phase of the mixture (NaCl/FeCl<sub>3</sub>) prepared in different mediums (in air, in water, and in 1,2-DCE). On the thermal desorption curves for the active phase of the catalysts for direct chlorination of ethylene (NaCl + FeCl<sub>3</sub> mechanical mixture), prepared by mixing (grinding) the solid crystals in air (Fig. 3a), residues from decomposition of the NaCl/FeCl<sub>3</sub> crystals show up clearly, and atomic chlorine (molecular mass of Cl 35-36) or molecular hydrogen chloride (molecular mass of HCl 36-38) are present. At the same time, the thermal desorption curves for decomposition of the melt of the active phase of the catalyst for the direct chlorination of ethylene (NaCl + FeCl<sub>3</sub> + H<sub>2</sub>O), prepared after drying from the aqueous solution (Fig. 3b), show residues from decomposition of water (molecular mass of H<sub>2</sub>O 16-18) and the crystal hydrates of the salts. The adsorption residues of the destructured ethylene of 1,2-DCE (molecular mass of C<sub>x</sub>H<sub>y</sub>Cl<sub>z</sub> 27-44) only appear on the thermal desorption curves for dissociation of the active phase of the catalyst for direct chlorination of ethylene (NaCl + FeCl<sub>3</sub> + DCE) obtained by drying from a solution in 1,2-DCE (Fig. 3c). It is clear that during preparation of the catalyst FeCl<sub>3</sub> and promoter NaCl in the 1,2-DCE medium intermediate

TABLE 2. Results of Investigation of the Mutual Dissolution of NaCl and FeCl<sub>3</sub> in 1,2-DCE for Direct Chlorination of Ethylene

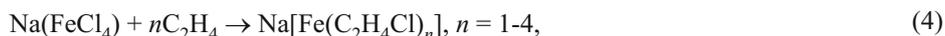
Expt. No.	Diameter of NaCl particles, μm	Dissolution temperature of catalyst, °C	Dissolution time of catalyst, h	Stirrer rotation rate, rpm	Concentration of NaCl			Concentration of FeCl <sub>3</sub>	
					given, ppm	determined by analytical method, ppm	determined by gravimetric method, ppm	given, ppm	analyzed, ppm
1	120	78	1.0	300	400	10.8	15.4	–	–
2	63	78	1.0	150	400	30.6	31.2	–	–
3	45	78	1.0	300	400	35.6	40.2	–	–
4	63	78	1.0	300	39.9	2.03	2.31	–	–
5	63	50	1.0	300	397	30.6	31.2	–	–
6	63	78	1.0	300	397	36.6	37.0	–	–
7	63	78	1.0	300	100	5.5	5.8	–	–
8	63	78	1.0	300	400	45.2	70	600	153
9	63	78	1.0	300	100	32	38	660	87
10	63	78	1.0	300	40	15	17	660	82
11	63	78	2.0	300	700	42	78	1000	558
12	63	78	1.0	300	100	12	39	1000	89
13	–	78	1.0	300	0	0	0	1000	421
14	–	78	1.0	Without stirring	0	0	0	1000	410
15	63	78	2.0	300	400	43.3	45	1000	323
16	63	78	2.0	300	100	30.5	32	1000	419
17	63	78	2.0	300	40	10	15	1000	467

nanocomplexes can be formed between them, and they can serve as catalysts for the direct chlorination of ethylene to 1,2-DCE. We therefore proposed a new structure for the catalyst and mechanism of this reaction described below.

Unlike the mechanism of reaction (1) described by the authors of [2] we consider that at the second stage the catalytic complex of FeCl<sub>3</sub> changes into a nanostructured catalytic complex of donor–acceptor type Na(FeCl<sub>4</sub>) with the NaCl (reactions (2), (3)), which interacts with ethylene according to reaction (4), wherein the regeneration of the catalyst and promoter proceeds according to the reaction (5) [6].

It must be expected that the process in the liquid dichlorethane medium takes place with the participation of the dispersed partly dissolved catalyst and promoter (FeCl<sub>3</sub>, NaCl) and also chlorine and ethylene, while the rate of the reaction between them is higher than in the reaction of these individual gaseous reagents with each other. The mechanism of the reaction involves the possible formation of transitional nanocomplexes of ferrate and dissolved ethylene (reactions (4), (5)), like the proposed mechanism of oxidative chlorination of ethylene [7]:





Together with the reactions occurring by an ionic mechanism, under unfavorable conditions, i.e., with increase of temperature  $\geq 373$  K (100 °C) and concentrations of catalyst and promoter, the free-radical process of substituted chlorination of ethylene to 1,1,2-trichloroethane (TCE) can occur. A radical mechanism of substituted chlorination of already formed 1,2-DCE to 1,1,2-trichloroethane is also possible [8]. Hydrogen chloride is formed in both cases, and this retards the production of dichloroethane by the ionic mechanism, contaminates the reaction medium, and leads to corrosion of the equipment. In addition, with an excess of chlorine and iron(III) chloride substitution of hydrogen in the dichloroethane can occur with the formation of trichloroethylene (TCEtl) and tetrachloroethylene. They are present in the obtained dichloroethane as side products [6].

To study the mechanism and determine the possible effect of the dispersity of the catalyst and promoter of the direct chlorination of ethylene we undertook an analysis [6] of the industrial stage of direct chlorination of ethylene with the aim to assemble statistical data on the actual concentrations of sodium chloride and iron(III) chloride in dichloroethane and the amount of microimpurities in the DCE. These data are presented in Table 1. As seen from the data in Table 1, with decrease in the concentration of the catalyst and promoter the purity of the dichloroethane increases from 99.13% to 99.26%. Here the concentration of unreacted ethylene and vinyl chloride in the impurities is reduced by almost half. At the same time, the concentration of carbon tetrachloride (CTC) and chloroform formed as side products of the direct catalytic chlorination of ethylene is significantly reduced.

To determine the effect of the particle size of the catalyst and promoter, their surface area, and the effectiveness of their distribution in the DCE we then investigated the solubility of sodium chloride in relation to the degree of grinding of the particles of NaCl in the laboratory ball mill. At the end of grinding the sodium chloride powder was unloaded from the mill and separated by spreading onto screens with apertures of 45, 65, and 120  $\mu\text{m}$ , respectively. The collected fractions were then dissolved under standard conditions in dichloroethane with heating and stirring. The results are presented in Table 2.

While varying the dissolution temperature of the sodium chloride in the range of 323-351 K (50-78 °C), we determined the variation of the concentration of the dissolved sodium chloride in dichloroethane (Table 2).

We also studied the effect of the intensity of agitation of the components during heat treatment in dichloroethane on their solubility; the results of the investigation are presented in Table 2.

In addition the mutual effect of sodium chloride and iron(III) chloride on dissolution in DCE was investigated under standard conditions ( $N = 300$  rpm, temperature 351 K (78 °C), particle size 63  $\mu\text{m}$ , and dissolution time 1 h). These results are also presented in Table 2.

Further investigations of the temperature dependence of the solubility of NaCl in 1,2-DCE showed (experiments 6-8) that with increase of temperature from 293 K (20 °C) to 323 K (50 °C) and 351 K (78 °C) the solubility of NaCl rose from 2.9 to 30.6 ppm and reached a maximum value of 36.6-37.0 ppm at 351 K (78 °C). In order to obtain more reliable data we investigated the effectiveness of dissolution of NaCl in relation to the intensity of agitation of crystalline NaCl in DCE. For this the dissolution was conducted with and without agitation ( $I = 150-300$  rpm) (Table 2, expts. 2, 10, 11).

Investigations were also conducted on the dependence of the solubility of the promoter of direct chlorination (NaCl) on the particle size. The results are presented in Table 2 and Fig. 3a-c. As seen from Fig. 3a, with decrease of the sodium chloride crystal size from 120 to 40  $\mu\text{m}$  the concentration of sodium chloride in the DCE increases accordingly from 10 to 35 ppm. This shows that the solubility of NaCl in DCE depends on the particle size and on the parameters of diffusion during dissolution.

We also investigated the temperature dependence of the solubility of the promoter of direct chlorination (NaCl). These data are presented in Fig. 4a. As seen from the relationship presented in Fig. 4b, the solution of the salt NaCl in DCE is increased by four times when the temperature is increased from 293 K (20 °C) to 351 K (78 °C). This confirms our assumption that the mechanism of dissolution of NaCl in DCE has complex physicochemical character. The data presented in Fig. 4c, which shows the dependence of the concentration of NaCl in DCE on the intensity of agitation during dissolution of the

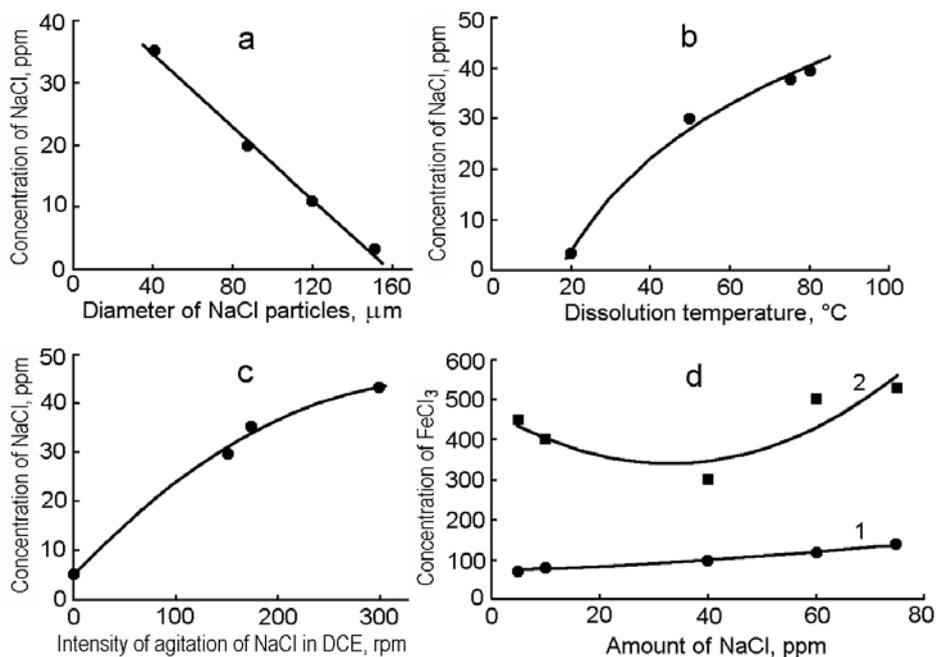


Fig. 4. Dependence of the concentration of NaCl on the diameter of the particles (a), the temperature (b), and the intensity of agitation during dissolution (c) of the promoter during direct chlorination of ethylene to 1,2-DCE at 78 °C and the dependence of the concentration of FeCl<sub>3</sub> on the amount of NaCl used for dissolution in dichloroethane at 351 K (78 °C) (d): 1) 1 h dispersion; 2) 2 h dispersion.

catalyst, lead to the same conclusion. As seen from the figure, the amount of dissolved (dispersed) NaCl in the DCE increases by more than four times during increase of the intensity of agitation.

Figure 4 shows the dependences of the mutual effect of the catalyst FeCl<sub>3</sub> and promoter NaCl during dissolution in DCE. As seen from Fig. 4d (curve 1), if the agitation time of the components is short (1 h), the concentration of dissolved FeCl<sub>3</sub> increases little with increase of the concentration of NaCl (from 50 to 100 ppm). This indicates that the complex between NaCl and FeCl<sub>3</sub> (NaFeCl<sub>4</sub>) is no longer formed under such conditions. At the same time, with increase of the intensity and duration (2 h) of agitation of the components (Fig. 4d, curve 2) the FeCl<sub>3</sub> undergoes chemical reaction with NaCl, and its concentration decreases from 450 to 350 ppm (Fig. 4d, curve 2). However, increase of the concentration of NaCl from 50 to 80 ppm then leads to some increase in the concentration of the catalyst FeCl<sub>3</sub> (to 500 ppm). It is clear that in the first case a catalytic nanocomplex is formed according to reaction (4) (NaFeCl<sub>4</sub>) and the concentration of pure FeCl<sub>3</sub> decreases, and direct chlorination with participation of the catalyst and promoter can then occur by the mechanism of reactions (2) and (3). If the concentration of the promoter is higher than equimolar (40-50 ppm), it no longer reacts with the FeCl<sub>3</sub>, and the concentration of pure FeCl<sub>3</sub> in the DCE increases, as reflected in the dissolution curves (Fig. 4d) and leads to significant increase in the concentration of FeCl<sub>3</sub>, to decrease in the yield of the main product 1,2-DCE, and to increase in the amount of the side products trichloroethane and tri- and tetrachloroethylene according to the mechanism of the substitution reaction (1). The same is observed with increase of the NaCl content. The ratio of NaCl to the weight of the catalytic complex amounts to 1 : 10. It is clear that the same ratio of NaCl and FeCl<sub>3</sub> concentrations can be obtained during dissolution in DCE, as is confirmed by the data in Table 2 and by the graphical relationships (Fig. 4d). In other words, the ratio of concentrations NaCl : FeCl<sub>3</sub> in DCE amounts to 50 : (500-1000) ppm, i.e., 1 : 10-20.

During analysis of the statistical data it was found that increase of the concentration of FeCl<sub>3</sub> above 800 ppm and that of NaCl above 50 ppm reduces the purity of the DCE and increases the amount of carbon tetrachloride, trichloroethane, and tri- and tetrachloroethylene microimpurities [6]. Increase of the temperature to 373 K (100 °C) and of the duration and intensity of

agitation and decrease of the particle size of the crystalline NaCl to 63  $\mu\text{m}$  or less increase the final concentration of NaCl and  $\text{FeCl}_3$  in the DCE by several times (Fig. 4a-d).

As a result of study of the mutual influence of NaCl and  $\text{FeCl}_3$  on their final concentration in the solution of 1,2-DCE it was established that an excess of NaCl (>400 ppm) on the dissolution has a negative effect on the final concentration of  $\text{FeCl}_3$  in the dichloroethane and reduces it to a certain extent, but this effect is levelled out by increase of the duration and intensity of dissolution. An excess of undissolved NaCl (~350 ppm) has a negative effect on the process and equipment and leads to corrosion of the latter and reduces the purity of the 1,2-DCE [2, 3, 5].

The investigations of the dependence of the solubility of sodium chloride and iron(III) chloride as catalysts of the direct chlorination of ethylene to 1,2-dichloroethane on the dispersity of the crystalline sodium chloride, the dissolution temperature, the intensity of agitation, and the mutual effect of the components of the catalyst showed a positive effect from all the above-mentioned parameters on the concentrations of sodium chloride and iron(III) chloride dissolved in the 1,2-DCE.

It was found that the direct chlorination of ethylene depends not only on the concentration of the catalyst, the promoter, and their complex ( $\text{NaFeCl}_4$ ) but also on the nature of its interaction with the ethylene and 1,2-dichloroethane. During the work the structure of the transitional complex of the catalyst and the promoter with ethylene and 1,2-dichloroethane ( $\text{Na}[\text{Fe}(\text{C}_2\text{H}_4\text{Cl})_4]$ ) was identified, and it was suggested that heterogeneous-homogeneous catalysis starts on the surface of the catalytic system and continues in the solution of 1,2-dichloroethane.

The investigations by DTA, X-ray diffraction, and mass-spectrometric analysis make it possible to propose a new metal-complex **mechanism** for the direct chlorination of ethylene (reactions (2)-(5)).

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