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The Behaviour of the System: Gelatin-Ferric Chloride-Neutral Electrolyte-Hydrochloric Acid or Sodium Hydroxide in an Aqueous Medium. II. The Behaviour of the Simpler System: Ferric Chloride -Sodium Hydroxide in an Aqueous Medium*

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The system $FeCl_3$-NaOH is one of the simpler systems composing the four component system gelatin-$FeCl_3$-NaCl-HCl or NaOH. The precipitation curve of the system $FeCl_3$-NaOH was systematically investigated.

Two types of the precipitation curve were found and discussed. First, the type with two separated maxima: the isoelectric maximum in the region of the equivalency of the components and the second one at high NaOH concentrations and high *p*H values, which appeared at low $FeCl_3$ concentrations. Second, the type with joined maxima, where the stable negative region between the maxima disappeared. This type appeared at high $FeCl_3$ concentrations. At intermediate $FeCl_3$ concentrations the transition type of the precipitation curve was found.

The summary diagrams represent the regions of the precipitation curve in dependence on the concentration of the components and the corresponding *p*H values. A schematic diagram represents the precipitation curve including the maximum of the slow hydrolysis.

The increasing age of the system caused: a) an increase of the turbidity of the negative stable region, b) the dissolution of the solid phase formed previously, c) the slow hydrolysis of the excess $FeCl_3$ after the systems had been prepared.

INTRODUCTION

We have already reported on the four component system gelatin-$FeCl_3$--NaCl-HCl or NaOH[1]. That system can be divided into simpler systems containing a lower number of components. In order to explain the phenomenology of the four component system, it is of interest to investigate the simpler systems separately. In this paper we report on our investigation of the two component system $FeCl_3$-NaOH covering a larger range of concentrations than previously reported[16].

$FeCl_3$ solution undergoes the process of slow hydrolysis at room temperature, forming a series of ferric complexes[2,3] and the solid phase β-FeOOH[4,5]. The rate of that process depends on the concentration of the $FeCl_3$ solution, on the acidity of the system, on the concentration of the solid phase formed during the process or added separately to the system, and on the presence of

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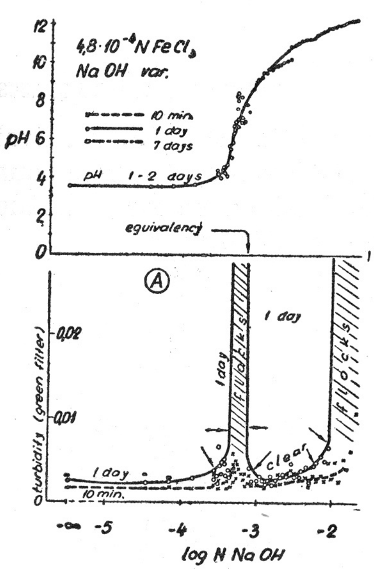


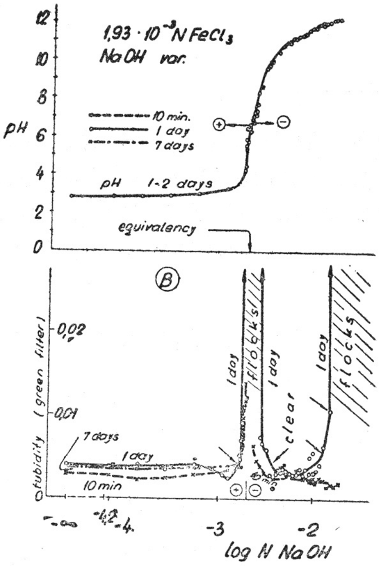
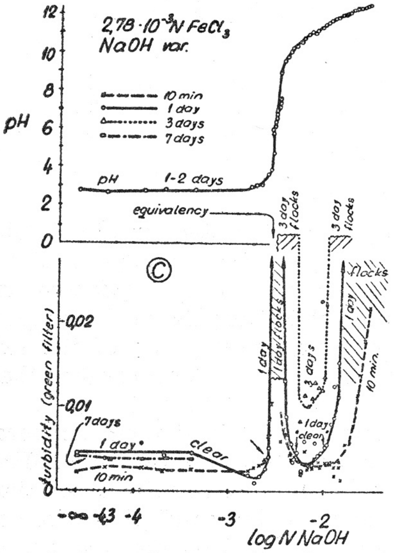


Fig. 1. System: $4.8 \cdot 10^{-4}N$ FeCl$_3$ — N NaOH varied. The precipitation curve with separated maxima.

Fig. 2. System: $1.93 \cdot 10^{-3}N$ FeCl$_3$ — N NaOH varied. The precipitation curve with separated maxima.



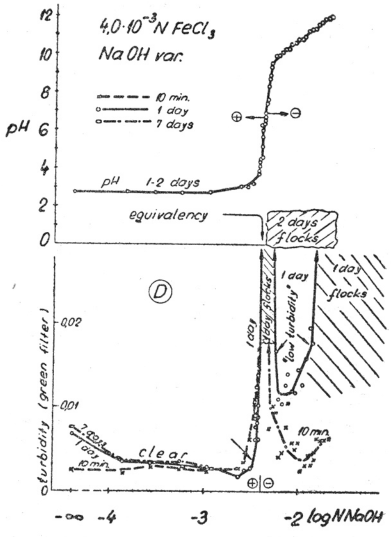
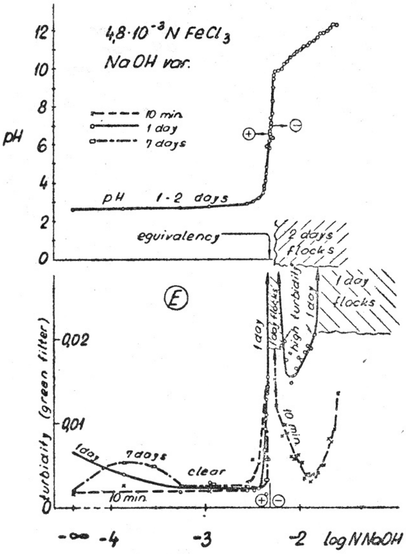


Fig. 3. System: $2.78 \cdot 10^{-3}N$ FeCl$_3$ — N NaOH varied. The precipitation curve with separated maxima.

Fig. 4. System: $4.0 \cdot 10^{-3}N$ FeCl$_3$ — N NaOH varied. The transition type of the precipitation curve.



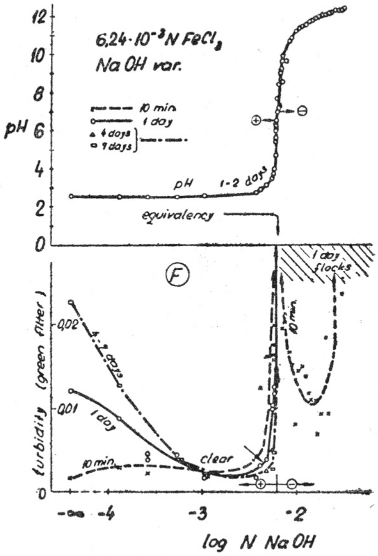
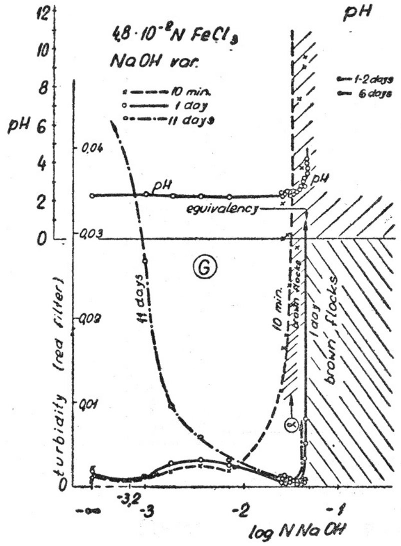


Fig. 5. System: $4.8 \cdot 10^{-3}N$ $FeCl_3$ — N NaOH varied. The transition type of the precipitation curve.

Fig. 6. System: $6.24 \cdot 10^{-3}N$ $FeCl_3$ — N NaOH varied. The precipitation curve with joined maxima.



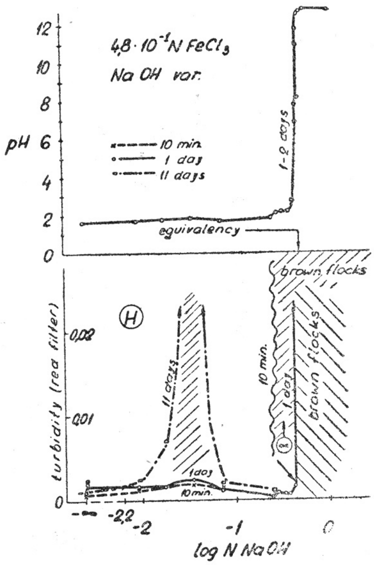
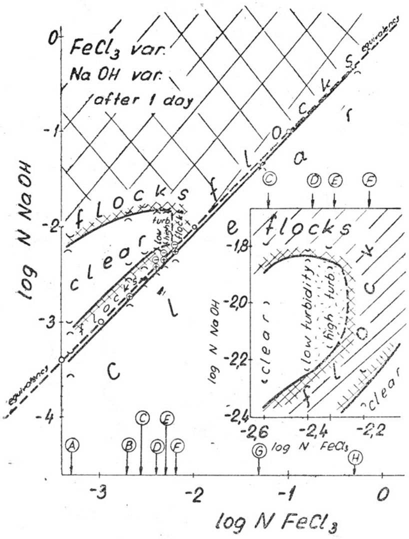


Fig. 7. System: $4.8 \cdot 10^{-2}N$ $FeCl_3$ — N NaOH varied. The precipitation curve with joined maxima.

Fig. 8. System: $4.8 \cdot 10^{-1}N$ $FeCl_3$ — N NaOH varied. The precipitation curve with joined maxima.



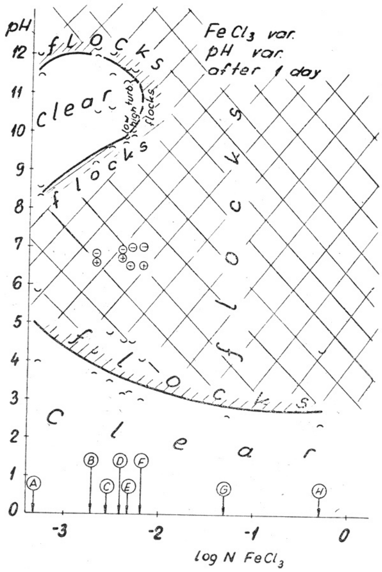


Fig. 9. System: N FeCl$_3$ varied — N NaOH varied.
The behaviour of the system in dependence of the concentrations of FeCl$_3$ and NaOH components.

Fig. 10. System: N FeCl$_3$ varied — N NaOH varied.
The behaviour of the system in dependence of the concentration of FeCl$_3$ component and pH value of the system.

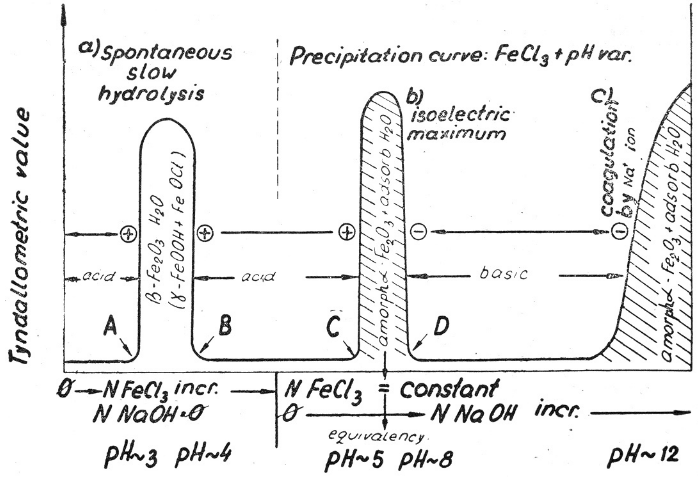


Fig. 11. Scheme of the precipitation curve of the system: FeCl$_3$ — pH, containing the region of slow hydrolysis of FeCl$_3$ solution at the room temperature and the region of the precipitation by addition of NaOH (the type of the precipitation curve with separated maxima).

some other substances (*e. g.* gelatin, agar, electrolyte)[6,7]. Several theories have been advanced concerning that problem. By the addition of OH^- ions to the solution of a ferric salt, a series of ferric complexes[2] and the solid phase, generally α-Fe_2O_3, are formed[8]. It is necessary to emphasize that the structure[9-12] and most of the properties of the solid phase are dependent on the conditions of its preparation and its age (*e. g.* electrokinetics[13], adsorption[14,15]).

By varying the concentrations of $FeCl_3$ and NaOH components systematically, the precipitation curve was obtained. The diagram turbidity *versus* concentration of one component, the other being constant, shows two maxima[16].

EXPERIMENTAL

We investigated the systems in the region from $4.8 \cdot 10^{-4}$ to $4.8 \cdot 10^{-1}$ *N* $FeCl_3$. Within each series, we varied the concentration of the NaOH component systematically, the concentration of the $FeCl_3$ component being kept constant. The concentration of the $FeCl_3$ component was changed from one series to the other.

The concentration of the components, calculated on the basis of the total volume after mixing, is expressed in normalities, one third of the molecular weight of $FeCl_3$ being taken as the equivalent weight.

The method of our experimental work, as described previously[1a], was modified. In order to prepare the systems, we added the NaOH solution to the $FeCl_3$ solution, poured the mixture back into the test tube of the NaOH component, repeating the procedure twice within an interval of 15 seconds. Immediately after each reading of the tyndallometric value (10 minutes, 1 hour and 1 day after the preparation of the system), the system was mixed in the same manner using a clean test tube.

At the lower concentrations of the $FeCl_3$ component ($4.8 \cdot 10^{-4}$ to $6.24 \cdot 10^{-3}$ *N*), we used a green filter for the tyndallometric measurements; at the higher concentrations ($4.8 \cdot 10^{-2}$ to $4.8 \cdot 10^{-1}$ *N*) we used a red filter because of the dark red colour of the systems.

RESULTS

Considering the precipitation curves obtained 1 day after the preparation of the systems, we found two distinct types.

In the concentration region from $4.8 \cdot 10^{-4}$ *N* $FeCl_3$ (A) to $2.78 \cdot 10^{-3}$ *N* $FeCl_3$ (C), we found a precipitation curve with two separated maxima designated as *flocks* (Figs. 1, 2 and 3). The first one (the left-hand one in Figs. 1, 2 and 3) was in the region of equivalency. The precipitation maxima were separated by the region of stable colloidal systems designated as *clear*. Stable colloidal systems with the concentration of the NaOH component lower than that of the $FeCl_3$ component (the left-hand side of the isoelectric maximum in Figs. 1, 2, 3) consisted of colloidal particles carrying positive electric charges. Stable colloidal systems with the concentration of the NaOH component higher than that of $FeCl_3$ (the right-hand side of the isoelectric maximum in Figs. 1, 2, 3) consisted of colloidal particles carrying negative electric charges. The flocks in the second precipitation maximum at high NaOH concentration (the right-hand maximum in the mentioned figures) were also characterised by the negative sign of their electric charges. If the concentration of the $FeCl_3$ component increased from $2.78 \cdot 10^{-3}$ *N* $FeCl_3$ (Fig. 3) to $6.24 \cdot 10^{-3}$ *N* (Fig. 6), the turbidity of the stable colloidal systems in the negative region (the region between the isoelectric maximum and the one on the right-hand side at high NaOH concentration) increased as represented on the 1 day curve in Fig. 4 (*low turbidity*) and Fig. 5 (*high turbidity*). This type of the precipitation curve ought to be considered as a transition type. (See the 1 day curves in Figs. 3—6, *clear-low turbidity-high turbidity-flocks*). In the concentration region of the $FeCl_3$ component from $6.24 \cdot 10^{-3}\,N\,FeCl_3$ (Fig. 6) to $4.8 \cdot 10^{-1}\,N\,FeCl_3$ (Fig. 8), the isoelectric maximum and that one on the right-hand side, at high NaOH concentration, were joined. The region of the negative stable systems between these two maxima disappeared and the precipitation curve consisted of only one maximum.

All the mentioned precipitation curves are summarized in Fig. 9. The region of *clear* stable colloidal systems, of *flocks,* and of *low* and *high* turbidities are represented in dependence on the concentration of the $FeCl_3$ and NaOH components in logarithmic scale. The dashed line represents the equivalency of the $FeCl_3$ and NaOH components. The electrophoretic data of the reversal of sign of the electric charge (isoelectric point) near the equivalency are marked in the figure. In the right-hand side od Fig. 9 the transition region is represented magnified. The arrows marked with capital letters in the diagram are placed corresponding to the concentrations of the $FeCl_3$ component in Figs. 1—8. The limits separating different regions in the diagram are not precisely known, the intervals being marked by parentheses.

In Fig. 10 the same experimental results are plotted using the logarithm of the concentration of the $FeCl_3$ component as the abscissa and the *p*H value of the system as the ordinate.

The described phenomena appeared 1 day after the preparation of the systems. By ageing, the turbidity on the negative stable region, the region *clear* between the two maxima, increased (compare the curves on the right-hand side of the isoelectric maximum corresponding to 10 minutes, 1 day and 3 days in Fig. 3; 10 minutes, 1 day and 2 days in Fig. 4; 10 minutes, 1 day and 2 days in Fig. 5; 10 minutes and 1 day in Fig. 6).

At higher concentrations of the $FeCl_3$ component ($4.8 \cdot 10^{-2}\,N\,FeCl_3$ in Fig. 7 and $4.8 \cdot 10^{-1}\,N\,FeCl_3$ in Fig. 8) we observed an opposite phenomenon. On the left-hand side of the isoelectric maximum, where the $FeCl_3$ component was present in a small excess, dense brown flocks appeared 10 minutes after the preparation. After one day the precipitate was dissolved yielding a dark red solution (α in Fig. 7, 8). The limit of the isoelectric maximum was shifted to higher concentrations of the NaOH component.

In the region of higher excess of the $FeCl_3$ component, the turbidity increased after prolonged time (compare the turbidity increase on the left-hand side of the curves corresponding to 1 day and 7 days in Figs. 5, 6 and 11 days in Figs. 7, 8.)

DISCUSSION

The precipitation curve with the separated maxima may be accepted as a general type showing the principal features of the system. The maxima in the precipitation curve, represented schematically by a), b) and c) in Fig. 11, are connected with different processes. The left-hand maximum a) is due to the process of slow hydrolysis of $FeCl_3$ solution (Ref. 16, Fig. 5). The isoelectric maximum b) and the maximum c) in Fig. 11 appear immediately or a short time after the system was prepared. We shall discuss these two maxima separately.

At low *p*H values iron is present in the form of Fe^{3+} ions or ferric complexes[3]. Increasing the *p*H value of the system, a series of ferric complexes is formed by the interaction of Fe^{3+} and OH^- ions[2]. When the solubility of the solid phase is exceeded[17], the solid phase precipitates. It is known that those constituent ions of the crystal lattice that are present in excess, are adsorbed on the surface of the solid phase charging the colloidal particles (*e. g.* Ag halo-

The difference in the feature of the diagram as well as the appearance of *gel, brown clumps, gel-flock* and *gel and brown flocks* are due to the specific action of the gelatin present.

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IZVOD

Vladanje sistema želatina-ferum(III)klorid-neutralni elektrolit-hidrogen klorid ili natrium hidroksid u vodenom mediju. II. Vladanje jednostavnijeg sistema ferum(III)klorid-natrium hidroksid

R. H. H. Wolf and B. Težak

Sistem $FeCl_3$ - NaOH jedan je od jednostavnijih sistema, koji grade sistem želatina - $FeCl_3$ - NaCl - HCl ili NaOH. Taložna krivulja sistema $FeCl_3$ - NaOH sistematski je istražena i razmotrena.

Postoje dva tipa taložne krivulje. Kod niskih koncentracija $FeCl_3$ javlja se tip s odijeljenim maksimumima: izoelektrični maksimum na području ekvivalence komponenata i drugi maksimum kod visokih koncentracija NaOH i visoke *p*H vrijednosti sistema (krivulja 1 dan na slici 1—3.). Kod visokih koncentracija $FeCl_3$ javlja se tip sa spojenim maksimumima, gdje je izostalo područje stabilnih negativnih sistema (krivulja 1 dan na slici 6. do 8.). Na području srednjih koncentracija $FeCl_3$ javlja se prelazni tip taložne krivulje (krivulja 1 dan na slici 4, 5.).

Sumarni diagrami prikazuju područja taložne krivulje u ovisnosti o koncentracijama komponenata i odgovarajućih *p*H vrijednosti sistema (slike 9. i 10.). Shematski diagram (slika 11.) prikazuje taložnu krivulju uključivo maksimum spore hidrolize.

Zapažena je uloga starosti sistema: a) porast mutnoće negativnoga stabilnog područja (slika 3, 4, 5.), b) otapanje prije već nastale krute faze (α na slici 7, 8.), c) spora hidroliza $FeCl_3$, koji je nakon taloženja krute faze preostao u suvišku (krivulje na lijevoj strani izoelektričnoga maksimuma na slikama 6. do 8., koje se odnose na sisteme veće starosti).

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