# 546.722-36:541.182.5:537.363

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

# Chloride-Sodium Chloride-Sodium Hydroxide in an Aqueous Medium\*

# R. H. H. Wolf and B. Težak

Laboratory of Physical Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia, Yugoslavia

## Received October 28, 1960

The system FeCl<sub>3</sub>-NaCl-NaOH is one of the simpler systems composing the four component system gelatin – FeCl<sub>3</sub>-NaCl-HCl or NaOH. It is formed by addition of the NaCl component to the system FeCl<sub>3</sub>-NaOH. The precipitation curve of the system FeCl<sub>3</sub>-NaOH consists of only one maximum. The coagulating action of  $6 \cdot 10^{-1} N$  NaCl causes the joining of two separate maxima occurring in the system with no NaCl added.

The summary diagrams represent the regions of the precipitation curve in dependence on the concentrations of the  $FeCl_3$  and NaOH components and the corresponding pH values.

At certain concentrations of the  $FeCl_3$  component, the precipitation maximum is extended far into the positive (acid) side.

#### INTRODUCTION

Considering the role of the neutral electrolyte NaCl in the phenomena occuring in the four component system gelatin-FeCl<sub>3</sub>-NaCl-HCl or NaOH<sup>1</sup>, it is of interest to investigate the influence of the NaCl component on the simpler system FeCl<sub>3</sub>-NaOH, as well as on the simpler systems containing the gelatin component. The behaviour of the system FeCl<sub>3</sub>-NaOH has been investigated<sup>2</sup>. In order to show the influence of the NaCl component on those systems, it is necessary to investigate the system FeCl<sub>3</sub>-NaOH.

#### EXPERIMENTAL

The method of our experimental work has already been described<sup>2</sup>.

Before mixing the solutions, the NaCl and NaOH components were placed into the same test tube. Electrophoretic measurements were not performed because of high electrolyte concentration in the systems.

#### RESULTS

All reported systems contained  $6 \cdot 10^{-1} N$  NaCl separately added to the system. The concentrations of the FeCl<sub>3</sub> component were the same as in the preceding paper<sup>2</sup> and marked by corresponding letters. In order to compare the results, the figures of the preceding paper on the system FeCl<sub>3</sub>-NaOH will be marked by II.

\* Contribution No. 90 from the Laboratory of Physical Chemistry. Reported at the I. Yugoslav Congress for Pure and Applied Chemistry, Zagreb, June 1960.

CCA-203



# Fig. 1. A) System: 4.8.10<sup>-4</sup> N FeCl<sub>3</sub>-6.10<sup>-1</sup> N NaCl-N NaOH varied. B) System: 1.93.10<sup>-8</sup> N FeCl<sub>3</sub>-6.10<sup>-1</sup> N NaCl-N NaOH varied. The precipitation curve with joined maxima. Fig. 2. C) System: 2.78 · 10<sup>-3</sup> N FeCl<sub>3</sub>-6 · 10<sup>-1</sup> N NaCl-N NaOH varied

 Fig. 2. C) System: 2.78 · 10<sup>-3</sup> N FeCl<sub>3</sub>-6 · 10<sup>-1</sup> N NaCl-N NaOH varied.
 D) System: 4.0 · 10<sup>-3</sup> N FeCl<sub>3</sub>-6 · 10<sup>-1</sup> N NaCl-N NaOH varied. The precipitation curve with joined maxima.





Fig. 3: E) System: 4.8 • 10<sup>-3</sup> N FeCl<sub>3</sub>-6 • 10<sup>-1</sup> N NaCl-N NaOH varied.
 F) System: 6.24 • 10<sup>-3</sup> N FeCl<sub>3</sub>-6 • 10<sup>-1</sup> N NaCl-N NaOH varied.
 The precipitation curve with joined maxima.

Fig. 4. G) System: 4.8 • 10<sup>-2</sup> N FeCl<sub>3</sub>-6 • 10<sup>-1</sup> N NaCl-N NaOH varied.
H) System: 4.8 • 10<sup>-1</sup> N FeCl<sub>3</sub>-6 • 10<sup>-1</sup> N NaCl-N NaOH varied. The precipitation curve with joined maxima.



- Fig. 5. System: N FeCl<sub>3</sub> varied- 6.10<sup>-1</sup> N NaCl-N NaOH varied. The behaviour of the system in dependence on the concentrations of FeCl<sub>3</sub> and NaOH components.
- Fig. 6. System: N FeCl<sub>2</sub> varied- 6.10<sup>-1</sup> N NaCl-N NaOH varied.
   The behaviour of the system in dependence on the concentration of FeCl<sub>2</sub> component and pH value of the system.



#### Fig. 7. System:

System: a) 4.8.10<sup>-3</sup> N Ft·Cl<sub>3</sub>- 4.4.10<sup>-5</sup> N HCl- 0 N NaCl-N NaOH varied. c) 4.8.10<sup>-3</sup> N FeCl<sub>3</sub>- 4.4.10<sup>-5</sup> N HCl- 6. 10<sup>-2</sup> N NaCl-N NaOH varied. b) 4.8.10<sup>-3</sup> N FeCl<sub>3</sub>- 4.4.10<sup>-5</sup> N HCl-4.4. 10<sup>-1</sup> N NaCl-N NaOH varied. The influence of NaCl component separately added into the system. From Figs. 1, 2, 3, 4 it is obvious that the precipitation curves of the system  $FeCl_3-6 \cdot 10^{-1} N$  NaCl-NaOH possess only one maximum.

By comparing the 1 day curves corresponding to the systems containing  $6 \cdot 10^{-1} N$  NaCl with the curves of the systems containing the same concentrations of the FeCl<sub>3</sub> component, but with no NaCl added (Fig. 1.B — Fig. 2/II, Fig. 2. D — Fig. 4/II, Fig. 3. E — Fig. 5/II), it can be noticed that the presence of  $6 \cdot 10^{-1} N$  NaCl causes the joining of the two precipitation maxima. The region of stable negative colloidal systems (*clear* in Figs. 1/II, 2/II, 3/II, *low turbidity* in Fig. 4/II, *high turbidity* in Fig. 5/II) disappeared if  $6 \cdot 10^{-1} N$  NaCl was added. At high concentration of the FeCl<sub>3</sub> component the systems with  $6 \cdot 10^{-1} N$  NaCl was added or without it, show the same type of the precipitation curve with joined maxima (compare Fig. 3. F — Fig. 6/II, Fig. 4. G — Fig. 7/II, Fig. 4. H — Fig. 8/II).

It can be seen that at the concentration of  $4.8 \cdot 10^{-4} N \text{ FeCl}_3$  the region of the precipitation maximum is extended far from the equivalency (flocks in Fig. 1. A). At the concentration of  $2.78 \cdot 10^{-3} N \text{ FeCl}_3$  the results are dispersed and no limiting curve was found (Fig. 2. C), but the lack of the negative stable region indicated the type of the precipitation curve with joined maxima.

Fig. 5 shows the behaviour of the system  $\text{FeCl}_3$ -6  $\cdot$  10<sup>-1</sup> N NaCl-NaOH in dependence on the concentration of the FeCl<sub>3</sub> and the NaOH components, and in Fig. 6 the same results are represented in dependence on the concentration of the FeCl<sub>3</sub> component and the *p*H value of the system (the limiting values lying between the parentheses). Comparing Fig. 5 — Fig. 9/II and Fig. 6 — Fig. 10/II it can be noticed that the region *clear* on the left-hand side of the equivalency in Figs. 9/II and 10/II disappeared in the presence of  $6 \cdot 10^{-1} N$  NaCl.

Fig. 7 shows the precipitation curve of the system 4.8  $\cdot$  10<sup>-3</sup> N FeCl<sub>3</sub>-N NaOH with:

a) no NaCl added,

b)  $4.4 \cdot 10^{-2} N$  NaCl added (corresponding to the concentration of Na<sup>+</sup> ions added by the NaOH component at the point A on the curve),

c)  $6 \cdot 10^{-1} N$  NaCl (concentration used in all systems represented in this paper).

The curve a) consists of two separated maxima, but the curves b) and c) consist of only one maximum (the type with joined maxima).

#### DISCUSSION

The discussion of our preceding paper<sup>2</sup> may be extended in this chapter.

Comparing the precipitation curves of the systems containing  $6 \cdot 10^{-1} N$  NaCl with those of the systems of the same FeCl<sub>3</sub> concentrations but with no NaCl, it is obvious that the presence of  $6 \cdot 10^{-1} N$  NaCl causes the joining of the maxima. We investigated the coagulating action of the neutral electrolyte upon the colloidal Fe(OH)<sub>3</sub> earlier (Ref. 3, Figs. 3, 4). In the systems FeCl<sub>3</sub>-NaOH at low FeCl<sub>3</sub> concentration with separated precipitation maxima, the addition of  $6 \cdot 10^{-1} N$  NaCl induces coagulation in the region of negative stable colloidal systems (*i. e.* the joining of the maxima) as well as the broadening of the isoelectric maximum on the side of positive (acid) stable systems (compare Fig. 5 — Fig. 9/II, Fig. 6 — Fig. 10/II). At high concentrations of the FeCl<sub>3</sub> component the coagulating action of NaCl separately added to the system is not marked, owing to the high concentration of NaCl formed by the reaction FeCl<sub>3</sub> + 3 NaOH  $\rightarrow$  Fe(OH)<sub>3</sub> + 3 NaCl, and perhaps owing to the high concentration of the solid phase Fe(OH)<sub>3</sub> formed.

# FERRIC CHLORIDE - SODIUM CHLORIDE - SODIUM HYDROXIDE

It was mentioned in our preceding paper<sup>2</sup> that the second precipitation maximum of the system  $\text{FeCl}_3$ -NaOH at a high NaOH concentration and a high pH value is due to the coagulating action of the Na<sup>+</sup> counterion on the negative colloidal particles  $\text{Fe(OH)}_3$ . That opinion may be supported by the experiment represented in Fig. 7. When  $4.4 \cdot 10^{-2} N$  NaCl is added separately to the system (corresponding to the Na<sup>+</sup> content added by NaOH at the point A), the colloidal systems in the negative stable region coagulate. The same effect is caused by the addition of a higher concentration of NaCl (6  $\cdot 10^{-1} N$ ).

It is of interest to compare the diagram in Fig. 6 with the diagram representing the systems containing the same components with  $0.425^{\circ}/_{0}$  gelatin added (Ref. 1a, Fig. 5, Ref. 1b, Fig. 7). The specific action of gelatin is responsible for the appearance of the region *clear* over a large *pH* interval (in spite of  $6 \cdot 10^{-1}$  N NaCl present) as well as for the appearance of the *white gel*, the orange gel, the brown clumps, the gelatin gel + Fe(OH)<sub>3</sub> flocks, and the transition phenomena high turbidity and low turbidity.

REFERENCES

a) R. Wolf and B. Težak, Croat. Chem. Acta 29 (1957) 461.
 b) B. Težak, R. Wolf, and S. Kratohvil, J. chim. phys. 55 (1958) 307.

2. R. H. H. Wolf and B. Težak, Croat. Chem. Acta 33 (1961) 1.

3. B. Težak and R. Wolf, Arhiv kem. 25 (1953) 39.

#### IZVOD .

### Vladanje sistema: želatina-ferum(III)klorid-neutralni elektrolit-hidrogen klorid ili natrium hidroksid u vodenom mediju. III. Vladanje jednostavnijega sistema: ferum(III)klorid-natrium klorid-natrium hidroksid u vodenom mediju

## R. H. H. Wolf i B. Težak

Sistem FeCl<sub>3</sub>-NaCl-NaOH jedan je od jednostavnijih sistema, koji grade četverokomponentni sistem želatina - FeCl<sub>3</sub>-NaCl-HCl ili NaOH, a nastaje dodatkom komponente NaCl u sistem FeCl<sub>3</sub>-NaOH.

Taložna krivulja sistema  $FeCl_3 - 6 \cdot 10^{-1} N NaCl-NaOH$  posjeduje samo jedan maksimum, koji je nastao sraštavanjem dvaju odijeljenih maksimuma kod sistema bez NaCl. Razmatrano je koagulaciono djelovanje  $6 \cdot 10^{-1} N NaCl$  komponente (slika 7), koje dovodi do spajanja dvaju odijeljenih maksimuma kod sistema bez te komponente.

Sumarni diagrami prikazuju područja taložne krivulje sistema  $FeCl_3 - 6 \cdot 10^{-1} N$ NaCl-NaOH u ovisnosti o koncentraciji  $FeCl_3$  i NaOH komponenata te o odgovarajućim *p*H vrijednostima sistema (slika 5, 6).

Kod nekih se koncentracija FeCl<sub>3</sub> komponente (slika 1.A) maksimum na taložnoj krivulji znatno proširio na pozitivnu (kiselu) stranu.

FIZIČKO-KEMIJSKI INSTITUT PRIRODOSLOVNO-MATEMATIČKI FAKULTET ZAGREB

Primljeno 28. listopada 1960.

13