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**The Behaviour of the System Gelatin — Ferric Chloride —  
Neutral Electrolyte — Hydrochloric Acid or Sodium Hydroxide  
in an Aqueous Medium.\* I.  
Phenomenology and the Method of Investigation by Division  
into Simpler Systems**

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The behaviour of the four-component system: gelatin —  $\text{FeCl}_3$  —  $\text{NaCl}$  (neutral electrolyte) —  $\text{pH}$  ( $\text{HCl}$  or  $\text{NaOH}$ ) was investigated. The regions of the gel formation, of the precipitation of brown  $\text{Fe}(\text{OH})_3$  flocks, of flocks and gel appearing together, and of the clear solution, were investigated and represented on a three-dimensional diagram (Fig. 13.). The gelatin concentration was kept at the constant value of 0.425%, but the concentrations of  $\text{FeCl}_3$ , the concentrations of  $\text{NaCl}$  and the  $\text{pH}$  values were varied and used as coordinates on Fig. 13.

Figs. 5, 9, 10, 11, 12 I, II, III, IV and 14 represent the systems where the concentration of one of the components was kept at a constant value. They are also represented on section planes on Fig. 13.

The rôle of each component in the behaviour of the four-component system is discussed. In order to explain these phenomena, the procedure for dividing the four-component system into simpler ones is shown. The latter will be studied separately.

#### INTRODUCTION

There are many papers dealing with the influence of gelatin on the behaviour of colloidal systems. The phenomena of sensitisation, of stabilisation and of complex coacervation have been investigated.

It can be said generally that a small amount of added gelatin or protein renders the hydrophobe sol more sensitive, while a greater one makes it more stable. There are many interpretations of such phenomena.

The small amount of added protein desorbs the stabilising  $\text{Fe}^{3+}$  ion from the  $\text{Fe}(\text{OH})_3$  particle and consequently decreases its stability. The greater amount of protein envelopes the particle and protects it from agglomeration (Fuks<sup>1</sup>, Lindau<sup>2</sup>).

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We call this system: gelatin —  $\text{FeCl}_3$  — neutral electrolyte —  $\text{pH}$ .

The polar groups of the gelatin molecules are adsorbed on the surface of  $\text{Fe}(\text{OH})_3$  particle. The hydrophobe hydrocarbon chains remain free and oriented towards the bulk of the solution. These chains adhere together and form a protecting layer around the particle (Abkin<sup>3</sup>). The agglomeration of the particles is due to the interaction of their unprotected surfaces (Lipatov<sup>4</sup>).

In connection with such conceptions it is of interest to mention another explanation of adsorption phenomena of gelatin on colloidal AgBr. In the first layer of the gelatin molecules round the sol particle, the polar groups of the gelatin molecules are oriented towards the surface of the particle. The remaining free hydrocarbon chains fuse together and join the particles (sensitisation). With a greater amount of the gelatin added, a second layer is formed round the first one, but in the second layer the gelatin molecules are oppositely oriented. The hydrocarbon chains of the second layer adhere to the hydrocarbon chains of the first one, and the polar groups form the surface of such an aggregate. The stability of the aggregate is due to the polar character of its surface (Sheppard, Lambert, Swinehart<sup>5</sup>).

It is to be noticed however, that the mentioned conceptions are not in accordance with the rôle of the hydrocarbon chains and of the polar groups of gelatin or of proteins in the processes concerned.

The phenomena of sensitisation and of stabilisation of the colloidal systems can also be explained in a similar way. The protein particles are supposed to be of a spherical shape. If a small amount of protein is added, the protein particle is enveloped in  $\text{Fe}(\text{OH})_3$  particles. Such an aggregate possesses a hydrophobe surface. The increased weight and the loss of the total electrical charge of the aggregate causes its sensibility to the electrolyte (NaCl). If a greater amount of protein is added, the surface of the aggregate contains hydrophilic protein particles which render the system stable (Pauli and Dessauer<sup>6</sup>).

In addition to the phenomenology mentioned above it is interesting to note that the gelatin as a protecting colloid prevents the process of coagulation of a sol by a neutral electrolyte, but does not hinder the process of crystallization (Kolthoff and O'Brien<sup>7</sup>). By the addition of gelatin to the system of silver halogenide in statu nascendi it is possible to distinguish the coagulation from the crystallization phenomena (Težak and Kratochvil<sup>8</sup>).

In these explanations the behaviour of the gelatin in dependence of the different conditions was not taken into account. It is known that gelatin precipitates the negative or the positive  $\text{Fe}(\text{OH})_3$  sol depending on the acidity of the medium<sup>9</sup>. The presence of an electrolyte increases the stabilisation and the precipitation power of gelatin<sup>10, 11, 6</sup>. It is known that the phenomena of complex coacervation depend upon the electric charge of the gelatin molecules, which again is connected with the pH value of the system<sup>12</sup>.

We wanted to get an insight into the factors governing the behaviour of our four-component system where the gelatin plays an important rôle. It is necessary to regard the systems as consisting of components which change their behaviour in accordance with the conditions. The behaviour of the whole system is dependent upon the mutual action of all the components. In this paper and those following it we are, therefore, discussing the behaviour of

our four-component system on the basis of separate investigations of simpler systems contained in them.

#### EXPERIMENTAL

##### 1. Preparation of the systems

The systems were prepared in the usual way<sup>13</sup>. Known volumes of aqueous solutions of the reaction components of known concentrations were put into the test tubes and the contents of the test tubes mixed. The concentrations of the components were calculated according to the total volume of the system after mixing.

The pH value of the system was varied by the addition of HCl or NaOH and this addition is designated as »pH«.

Care was taken that the solutions put into the same test tube did not react before mixing. In our four-component system: gelatin — FeCl<sub>3</sub> — NaCl — pH the disposition of the components in the test tubes was as follows: I. test tube: gelatin; II. test tube: FeCl<sub>3</sub>; III. test tube: NaCl+(HCl or NaOH)+H<sub>2</sub>O. To obtain a uniform mixture the contents of the test tubes were mixed by the following sequence: III-I-III-I-II-III-II-III-II-III-I-II.

##### 2. Preparation of the solutions

Analytical grade substances were used and dissolved in redistilled water. The concentrations of the components are expressed in normalities (*N*), while the concentration of gelatin is expressed in weight percents (wt. %).

The solutions of FeCl<sub>3</sub> or Fe(NO<sub>3</sub>)<sub>3</sub> were diluted immediately before the preparation of the systems from a stock solution of 4 *N* FeCl<sub>3</sub> or 1 *N* Fe(NO<sub>3</sub>)<sub>3</sub> containing a hundred times smaller amount of HCl or HNO<sub>3</sub> respectively to prevent the slow hydrolysis of the stock solution attended by the sol formation.

The solution of gelatin was prepared by swelling a weighed amount in water for half an hour and dissolving it at the temperature of 40–50°C. For each series of systems a fresh solution of 0.88% gelatin was prepared and diluted, through the addition of other components, to a final concentration of 0.425%. The low turbidity of the gelatin solution was neglected.

We used air-dry gelatin from »Tovarna kleja, Ljubljana« with 1.471% ash content\*. Some examinations were made with two other samples of gelatin containing 2.5% and 1.15% of ash, but the results showed no difference.

##### 3. Tyndallometric measurements

The tyndallometric measurements were made by a Zeiss-tyndallometer in combination with a Pulfrich-photometer in green light under the angle 135°.

##### 4. pH measurements

The pH measurements were made by a Macbeth-pH-meter with a glass electrode of high resistance. The buffer solutions served to obtain the gauge diagram (the plot of the true pH value against the pH value read on the scale of the instrument).

##### 5. Electrophoretic measurements

The electrophoretic measurements were made by the ultramicroscopic method using a double cell with a circular cross section to avoid the disturbances by the electroosmotic flow<sup>14</sup>. The particles of the sol were illuminated sideways through a split and observed at the right angle through a microscope consisting of an objective 10:1 (*A*=0.25) and an ocular 17X containing a gauged net.

The cell contained two electrodes on its ends with the known distance *l* between them, connected to the potential source with potential difference *V*. The direction of the electrical field was known. The sign of the electrical charge of the particle was determined by observing the direction of its migration under the influence of the electrical field. After including the automatic commutator the

\* E. Matijević, private communication.

field was commutated, a zigzag motion of the particle was observed and the distances  $d$  were determined by the gauged net in the ocular. The known value of the frequency of commutation gave information about the time of one half — period  $T_{1/2}$ , connected with the migration of the particle in one direction before the next commutation. By means of the known values  $d$ ,  $V$ ,  $l$  and  $T_{1/2}$  we calculated the electrophoretic mobility  $w$

$$w = \frac{d/T_{1/2}}{V/l} \cdot \frac{\text{Volt/cm.}}{\mu/\text{sec.}}$$

In our diagrams the curves of electrophoretic mobility are represented on a logarithmic scale.

The electrophoretic apparatus was made in our institute by Mirko Tkalčec using a Reichert microscope.

### 6. Temperature

The systems were kept at 20°C by means of a thermostat.

### RESULTS

We began our investigation by studying the phenomena of coagulation of  $\text{Fe}(\text{OH})_3$  sol in statu nascendi by addition of a neutral electrolyte (containing no ion constituent of the crystal lattice). It was shown that  $\text{Fe}(\text{OH})_3$  sol behaved like a hydrophobe sol and partially confirmed the rule of Schulze-Hardy<sup>15</sup>. It was interesting to investigate the behaviour of these systems in the presence of gelatin. We prepared a series of systems of positive  $\text{Fe}(\text{OH})_3$  sol in statu nascendi of the following composition:

$6.2 \times 10^{-3} N \text{ FeCl}_3 + 6.2 \times 10^{-3} N \text{ HCl}$   
 $5.0 \times 10^{-3} N \text{ NaOH}$   
 0.425% gelatin  
 $\text{KNO}_3$  varied, represented on Fig 1-A.

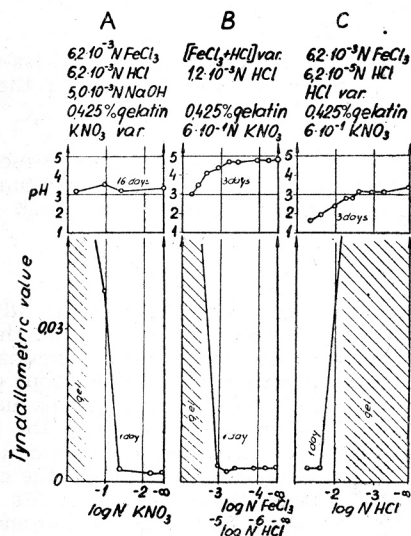


Fig. 1. Determination of »parameters« governing the gel formation.



We were faced with an interesting phenomenon. In earlier investigated systems without gelatin we obtained precipitates of red-brown flocks but in the system mentioned above we obtained a turbid thixotropic gel. We were of the opinion that this was a salting-out effect of gelatin caused by the high concentration of  $\text{KNO}_3$ . The next step was to try to produce the gel in the systems with high concentration of  $\text{KNO}_3$ , but with no  $\text{FeCl}_3$ :

0.425% gelatin  
 $6 \times 10^{-1} N \text{KNO}_3$   
 pH varied from 1.45 to 9.80 (by the addition of HCl or NaOH).

The gel formation was not noticed in spite of the great interval of pH value. This was obviously not a simple salting-out effect of gelatin, see Fig. 1-A, because the  $6.2 \times 10^{-3} N \text{FeCl}_3$  concentration was very small in comparison with the  $6 \times 10^{-1} N \text{KNO}_3$  concentration. The presence of  $\text{FeCl}_3$  had a specific influence upon the gel formation.

We wanted to find out the factors governing the gel formation and prepared the series:

$\text{FeCl}_3$  varied  
 $1.2 \times 10^{-3} N \text{HCl}$  (under very small variation, see the abscissa on Fig. 1-B)  
 0.425% gelatin  
 $6 \times 10^{-1} N \text{KNO}_3$ , represented on Fig. 1-B,  
 and:  $6.2 \times 10^{-3} N \text{FeCl}_3 + 6.2 \times 10^{-5} N \text{HCl}$   
 HCl varied (i. e. pH varied)  
 0.425% gelatin  
 $6 \times 10^{-1} N \text{KNO}_3$ , represented on Fig. 1-C.

Figs. 1-A, 1-B and 1-C show that the concentration of  $\text{KNO}_3$ , the concentration of  $\text{FeCl}_3$  and the pH value play the role of »parameters« governing the gel formation attended by the turbidity of the system.

Before further investigation we wanted to reduce the complications likely to appear in such a complex system. We therefore chose a neutral electrolyte to obtain a system with the possibly lowest number of ion species. NaCl was chosen because  $\text{Na}^+$  ion had also to be added by the addition of NaOH (regulation of pH value), and  $\text{Cl}^-$  ion by the addition of HCl (regulation of pH value) as well as by the addition of  $\text{FeCl}_3$ .

Using gelatin,  $\text{FeCl}_3$ , NaCl and pH (i. e. HCl or NaOH) as components, we began with systematical investigations. To find out the influence of one parameter on the behaviour of the system, it is necessary to change its value systematically, keeping the values of the other parameters constant. In the same way we investigated systematically the influence of each parameter.

Each letter of Table I represents one series of systems. It is evident that the concentration of NaCl was constant ( $6 \times 10^{-1} N$ ) in the series A, B, C, D, E, F, H and I. The concentration of  $\text{FeCl}_3$ , constant in the same series, changed from one series to another. The pH value was changed inside each series.

On Fig. 2 and 3 these systems are graphically represented. It is obvious that by the lowering the  $\text{FeCl}_3$  concentration the type of curve is changed.

TABLE I  
 0.425% gelatin

N NaCl \ N FeCl <sub>3</sub>	N FeCl <sub>3</sub>							
	$4.8 \times 10^{-1}$	$4.8 \times 10^{-2}$	$1.66 \times 10^{-2}$	$1.30 \times 10^{-2}$	$1.00 \times 10^{-2}$	$4.8 \times 10^{-3}$	$1.30 \times 10^{-3}$	$1.15 \times 10^{-3}$
$6 \times 10^{-1}$	A	B	C	D	E	F	H	I
$2.5 \times 10^{-1}$		P				U		
$6 \times 10^{-2}$	M	R				V		
$6 \times 10^{-3}$	N					W		
0	O	T				Z		

The curves A and C on Fig. 2 represent the first characteristic type. On the acid side (left) one can notice a sharp boundary limiting the region of

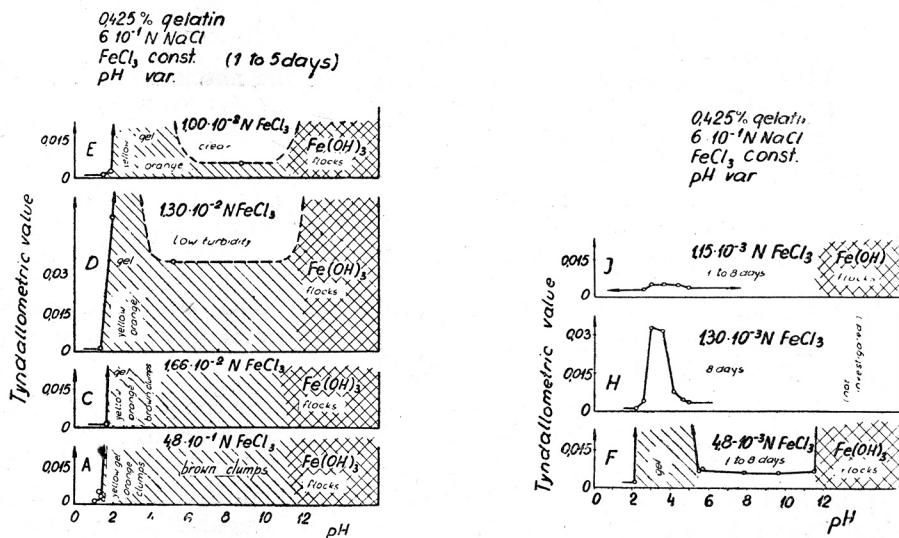


Fig. 2. System: 0.425% gelatin —  $6 \times 10^{-1} N$  NaCl — FeCl<sub>3</sub> constant — pH varied. Types of precipitation curve. These diagrams were used for the construction of Fig. 5.

Fig. 3. System: 0.425% gelatin —  $6 \times 10^{-1} N$  NaCl — FeCl<sub>3</sub> constant — pH varied. Types of precipitation curve (continuation). These diagrams were used for the construction of Fig. 5.

homogeneous yellow gel. By further increase of the pH value the gel became orange, then the gel clumps and brown flocks appeared together («brown clumps»), and at high pH value (right) the brown flocks, like these of Fe(OH)<sub>3</sub>, precipitated in the clear solution. We call these brown flocks: Fe(OH)<sub>3</sub>, but the possibility of this precipitate containing some admixtures should not be excluded.

By lowering the FeCl<sub>3</sub> concentration to  $1.30 \times 10^{-2} N$ , a «shallow» minimum appears (D on Fig. 2) designated as «low turbidity». When the lowering of FeCl<sub>3</sub> concentration progresses, the minimum becomes deep (E on Fig. 2. as well as F on Fig. 3) designated as «clear». The continuous deepening of that

minimum is shown on Fig. 4 representing the curves C, D and E. The corresponding minima at D and E are denoted in the same way, and the corresponding position on the curve without any minimum is denoted as »high turbidity«.

By the further lowering of FeCl<sub>3</sub> concentration the region of gel formation becomes smaller at the concentration 1.30 × 10<sup>-3</sup>N FeCl<sub>3</sub>, its maximum gets lower and narrower (curve H on Fig. 3) and finally disappears at the concentration 1.15 × 10<sup>-3</sup>N FeCl<sub>3</sub> (curve I on Fig. 3).

The region of Fe(OH)<sub>3</sub> flocks does not change. It is obvious that if the concentration of FeCl<sub>3</sub> approaches zero, the region of the Fe(OH)<sub>3</sub> flocks should disappear.

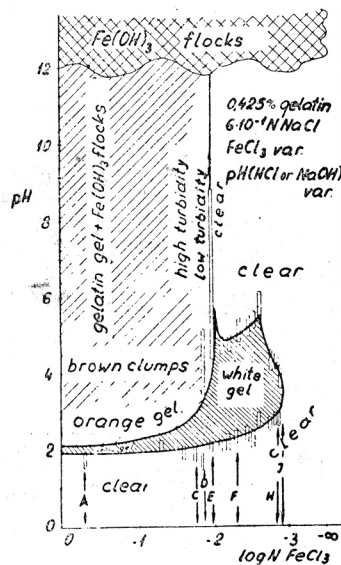
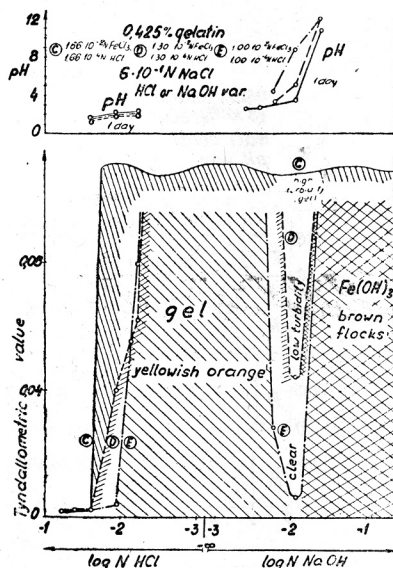


Fig. 4. System: 0.425% gelatin — 6 × 10<sup>-1</sup>N NaCl — FeCl<sub>3</sub> constant — pH varied. Transition curve type (D) between precipitation curve with separated maxima (E) and curve with joined maxima (C).

Fig. 5. System: 0.425% gelatin — 6 × 10<sup>-1</sup>N NaCl — FeCl<sub>3</sub> varied — pH varied. The behaviour of the system is the function of the parameters: normal concentration FeCl<sub>3</sub> (log scale) and pH value.

The dashed curves at D and E on Fig. 2 are not investigated in detail, but they are of the same type as curve F on Fig. 3.

Fig. 5 summarises the behaviour of the represented system containing 0.425% gelatin, 6 × 10<sup>-1</sup>N NaCl, with the FeCl<sub>3</sub> concentration and the pH value varied.

One parameter, represented by the FeCl<sub>3</sub> concentration, is plotted against the second one, i.e. the pH value. The different regions, separated by the curves, are visible. The limiting lines are not drawn precisely, the intervals being marked by small rectangles. One side of the rectangle is placed in one region, the other side in the neighbouring one, and the true limit is to be found between them. For the construction of Fig. 5 some other series, not represented here, were also used.

In the following experiments we prepared the series of vertical columns of Table I. The concentration of  $\text{FeCl}_3$  was constant in each column. The concentration of  $\text{NaCl}$  was constant in the same series, but changed from one series to the other. The pH value was changed from one system to the other in the same series.

Fig. 6 represents the column *F*, *U*, *V*, *W* and *Z* on Table I at the concentration  $4.8 \times 10^{-3} \text{N FeCl}_3$ . The curves are of the type where the maximum of gel formation and the maximum of  $\text{Fe(OH)}_3$  flocks are separated. By lowering the concentration of  $\text{NaCl}$ , the limit of the gel region on the acid side (left) shifts towards the higher pH values. It must be pointed out that the lowering of the  $\text{NaCl}$  concentration produces a change in the character of the gel

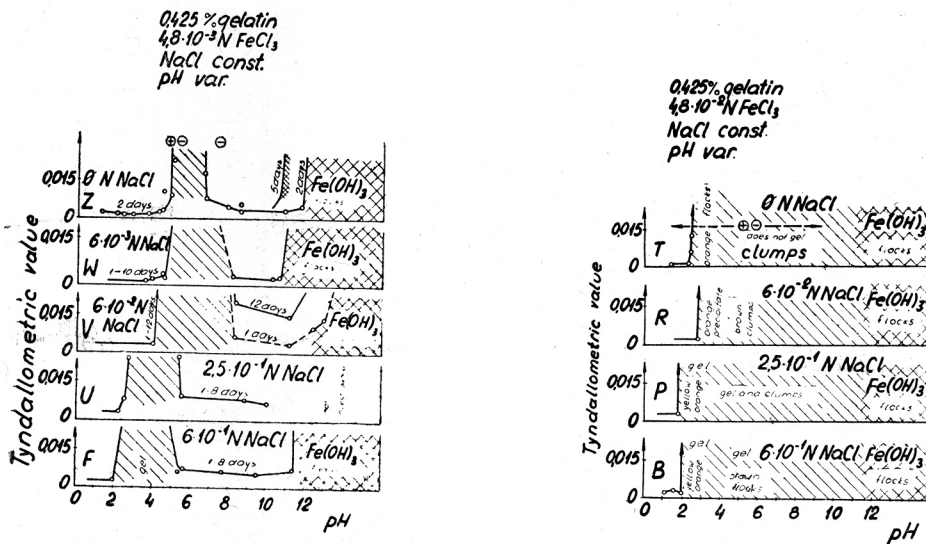


Fig. 6. System: 0.425% gelatin —  $4.8 \times 10^{-3} \text{N FeCl}_3$  —  $\text{NaCl}$  constant — pH varied. Types of precipitation curve. These diagrams were used for the construction of Fig. 9.

Fig. 7. System: 0.425% gelatin —  $4.8 \times 10^{-2} \text{N FeCl}_3$  —  $\text{NaCl}$  constant — pH varied. Types of precipitation curve. These diagrams were used for the construction of Fig. 10.

formed. At the concentration of  $6 \times 10^{-1} \text{N NaCl}$  (*F* on Fig. 6) a strong yellow-white thixotropic gel is formed. In the systems without  $\text{NaCl}$  (*Z* on Fig. 6) some large, frail, nearly transparent flocks, swimming in the bulk of the clear solution, are found, showing only little of the gel properties. We call this »gel flock«.

Fig. 7 represents the column *B*, *P*, *R* and *T* at the concentration  $4.8 \times 10^{-2} \text{N FeCl}_3$ .

The curves are of the type where the maximum of the gel formation and the maximum of  $\text{Fe(OH)}_3$  flocks have joined, the minimum between them having disappeared. By the lowering of the concentration of  $\text{NaCl}$ , the limit of the gel formation region on the acid side (left) shifts a little towards the higher pH value. The change of character of the gel is not so great as in the systems on Fig. 6.

Fig. 8 represents the column A, M, N and O on Table I at the concentration  $4.8 \times 10^{-1} N$   $FeCl_3$ .

The limit of the gel region on the acid side (left) does not change its position significantly by the change of the NaCl concentration. The character of the gel does not change.

On Figs. 9, 10 and 11 we summarize the behaviour of the systems shown on Figs. 6, 7 and 8 representing them on the diagrams where the NaCl concentration and pH value are used as coordinates. Some other series of the systems, not represented here, were also used for the construction of these diagrams. Fig. 9 represents the curve type where the maximum of gel formation is separated from the maximum of  $Fe(OH)_3$  flocks, Figs. 10 and 11 represent the

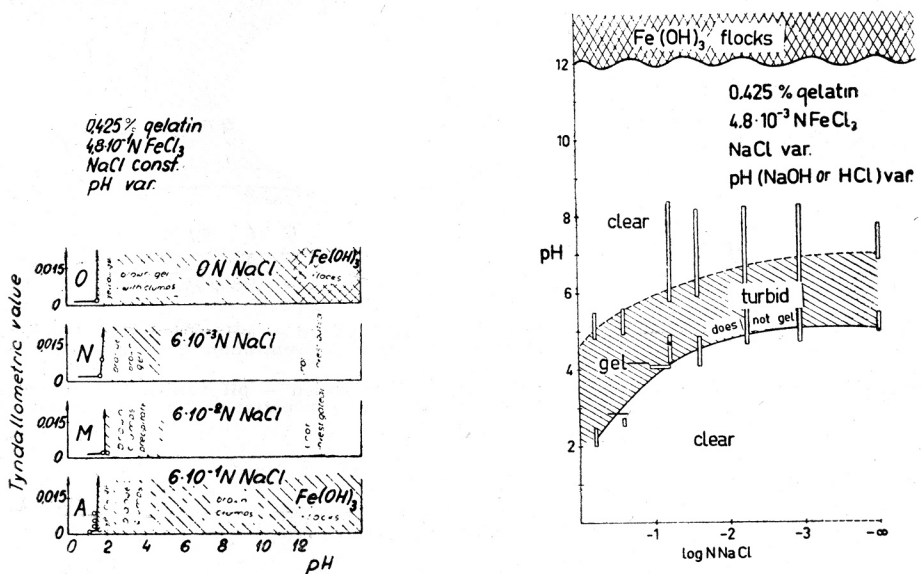


Fig. 8. System: 0.425% gelatin —  $4.8 \times 10^{-1} N$   $FeCl_3$  — NaCl constant — pH varied. Types of precipitation curve. These diagrams were used for the construction of Fig. 11.

Fig. 9. System: 0.425% gelatin —  $4.8 \times 10^{-3} N$   $FeCl_3$  — NaCl varied — pH varied. The behaviour of the systems is the function of the parameters: normal concentration NaCl (log scale) and pH value.

curves where these maxima are joined. The middle curve on Fig. 9 is dashed because of great differences in pH values between neighbouring systems in the series, but the curve type can be seen plainly. A more precise variation of the pH value by a careful addition of HCl or NaOH can lower the intervals containing the true limit.

If we compare the series N, W, M, R, V, P, U of the horizontal columns of Table I with the series A, B, C, D, E, F, H, I (from Fig. 5), we obtain the curves on Fig. 12.

At lower  $FeCl_3$  concentrations the limiting line between the gel formation region («turbid») and the clear solution is shifted towards a higher pH value (I, II, III and IV on Fig. 12).

In all the systems mentioned above the gelatin concentration after the mixing was 0.425%. The concentrations of the other three components were

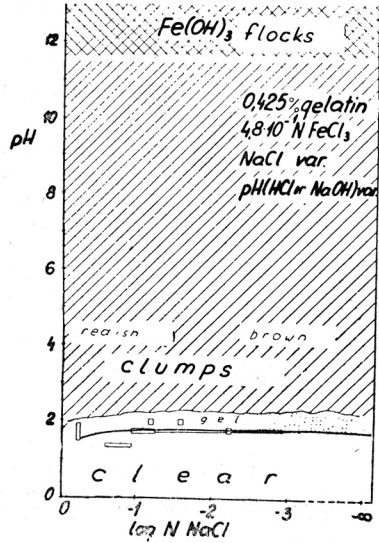
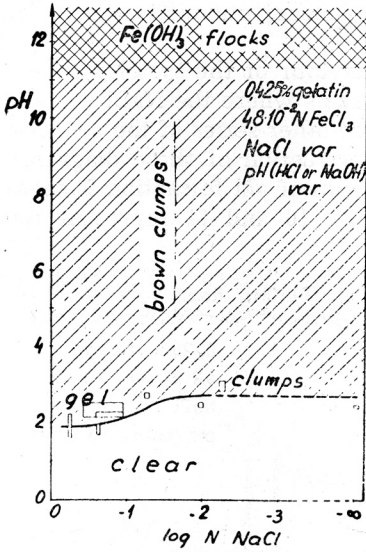


Fig. 10. System: 0.425% gelatin —  $4.8 \times 10^{-2} N \text{FeCl}_3$  — NaCl varied — pH varied. The behaviour of the system is the function of the parameters: normal concentration NaCl (log scale) and pH value.

Fig. 11. System: 0.425% gelatin —  $4.8 \times 10^{-1} N \text{FeCl}_3$  — NaCl varied — pH varied. The behaviour of the system is the function of the parameters: normal concentration NaCl (log scale) and pH value.

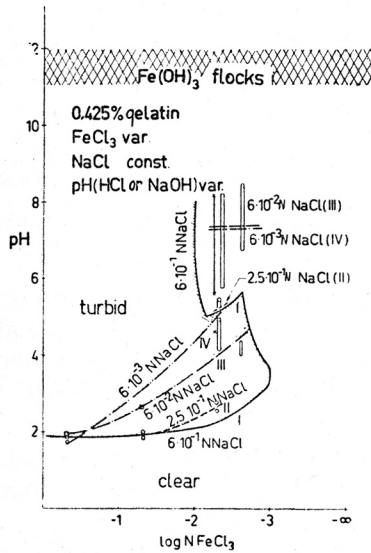


Fig. 12. System: 0.425% gelatin — NaCl constant —  $\text{FeCl}_3$  varied — pH varied. The behaviour of the system is the function of the parameters: normal concentration  $\text{FeCl}_3$  (log scale) and pH value for various NaCl concentrations (I, II, III, IV).

changed systematically (Table I) and the behaviour of the corresponding systems was investigated. We consider the concentrations of components to be the parameters deciding the behaviour of the system. Fig. 13 represents the four-component system: gelatin —  $\text{FeCl}_3$  —  $\text{NaCl}$  — pH in dependence of its parameters, used as coordinates in the three-dimensional diagram.

The systems did not change essentially during the time intervals from 1 day to about 9 days. The results obtained in those time intervals were used to construct our diagrams on Figs. 5, 9, 10, 11, 12, 13, 14. Later the gel formed in the system shows sometimes the phenomena of syneresis. The volume of

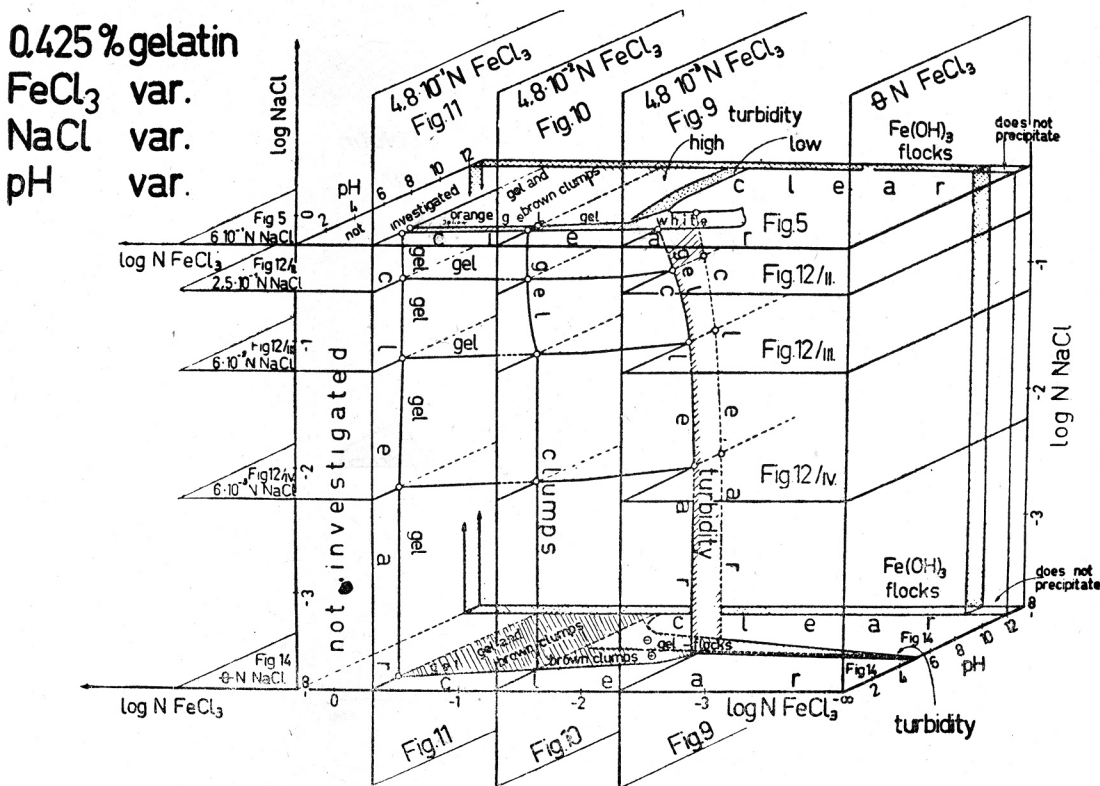


Fig. 13. System: 0.425% gelatin —  $\text{FeCl}_3$  varied —  $\text{NaCl}$  varied — pH varied. The behaviour of the system is shown on the three-dimensional diagram as the function of parameters: normal concentration  $\text{FeCl}_3$  (log scale), normal concentration  $\text{NaCl}$  (log scale) and pH value. Figs. 5, 9, 10, 11, 12, 14 are shown on section planes.

the gel decreases and becomes finally similar to a dense compact clump with a separated clear liquid.

It is to be emphasized that the value of the  $\text{NaCl}$  concentration on the diagrams represents only the amount of  $\text{NaCl}$  separately added into the systems. The amounts of  $\text{Na}^+$  ions and  $\text{Cl}^-$  ions brought into the systems by regulation of the pH value (through addition of  $\text{NaOH}$  or  $\text{HCl}$ ), as well as the amount of  $\text{NaCl}$  formed by the reaction  $\text{FeCl}_3 + 3 \text{NaOH} \rightarrow \text{Fe(OH)}_3 + 3 \text{NaCl}$  are not marked on the figures, but will be taken into account in the discussion.



The regions on the three-dimensional diagram on Fig. 13 are limited by surfaces. On the section planes, where the corresponding parameter is constant, one can see the diagrams from Figs. 5, 12 II, III, IV, 9, 10 and 11 oriented to form the three-dimensional coordinate system. The systems, where one of the components is at the concentration zero ( $0\text{ N FeCl}_3$  represented on the right vertical plane, and  $0\text{ N NaCl}$  represented on the bottom-horizontal plane, Fig. 14), belong to the simpler systems and will be discussed in one of our following publications. To complete Fig. 13 we have to show Fig. 14 separately, which represents the simpler system: gelatin —  $\text{FeCl}_3$  — pH.

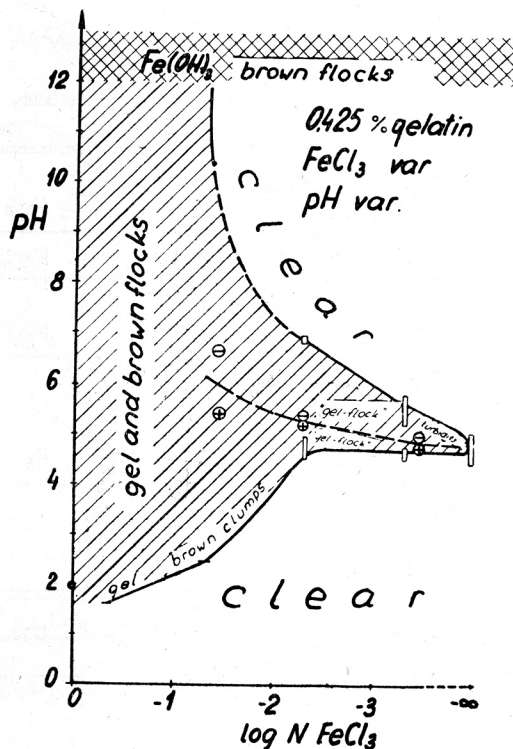


Fig. 14. System: 0.425% gelatin —  $\text{FeCl}_3$  varied — pH varied. The behaviour of the system is the function of parameters: normal concentration  $\text{FeCl}_3$  (log scale) and pH value.

#### Comparison with the behaviour of some analogous systems

In order to compare our systems with some analogous ones, we changed certain components in our system. To avoid the possibility of  $\text{Fe}^{3+}(\text{Cl})_n$  complexes<sup>16</sup> we used  $\text{Fe}(\text{NO}_3)_3$  instead of  $\text{FeCl}_3$ , and  $\text{NaNO}_3$  instead of  $\text{NaCl}$ . We used  $\text{AlCl}_3$  instead of  $\text{FeCl}_3$  and changed the neutral electrolyte as well. In the systems:

0.425% gelatin —  $4.8 \times 10^{-3}\text{ N Fe}(\text{NO}_3)_3$  —  $6 \times 10^{-1}\text{ N NaNO}_3$  — pH ( $\text{HNO}_3$  or  $\text{NaOH}$  varied),

and: 0.425% gelatin —  $4.8 \times 10^{-3}\text{ N Fe}(\text{NO}_3)_3$  —  $6 \times 10^{-1}\text{ N Na}_2\text{SO}_4$  — pH ( $\text{H}_2\text{SO}_4$  or  $\text{NaOH}$ ) varied

we observed (inside the experimental error) the same behaviour as at  $F$  on Fig. 5, which contained the same  $\text{Fe}^{3+}$  ion concentration.

In analogous systems:

0.425% gelatin —  $4.8 \times 10^{-3}N$   $\text{AlCl}_3$  —  $6 \times 10^{-1}N$  NaCl — pH (HCl or NaOH) varied,

and: 0.425% gelatin —  $4.8 \times 10^{-3}N$   $\text{AlCl}_3$  —  $6 \times 10^{-1}N$  KCNS — pH (HCl or NaOH) varied

we found that the use of  $\text{AlCl}_3$  instead of  $\text{FeCl}_3$  of the same concentration shifts the litiming region of the gel formation to the higher pH values. The difference was more than one pH unit in comparison with  $F$  on Fig. 5.

The gel was also formed in the system where  $\text{Th}(\text{NO}_3)_4$  had been used instead of  $\text{FeCl}_3$ , but the gel formation did not appear in the systems where  $\text{MgCl}_2$  had been used instead of  $\text{FeCl}_3$ . Before answering if  $\text{MgCl}_2$  could cause the gel formation in such systems, it would, however, be necessary to investigate the behaviour of this system by systematical variation of the parameters.

We wanted to know if a nonelectrolyte could provoke the gel formation effect if used instead of »neutral electrolyte«. We chose saccharose.

In the system analogous to  $F$  on Fig. 5:

0.425% gelatin —  $4.8 \times 10^{-3}N$   $\text{FeCl}_3$  —  $6 \times 10^{-1}M$  saccharose — pH ( $\text{HNO}_3$  or NaOH) varied

the gel formation did not appear. We observed only an isoelectric maximum which appeared without saccharose also in the simpler system: gelatin —  $\text{FeCl}_3$  — pH. It is obvious that the electrolytic nature of added component is responsible for the gel formation.

For the »neutral electrolyte« we chose such one that forms no solid phase if added to other components. It would therefore be needless to investigate the system: neutral electrolyte — pH. But to exclude the possibility that the observed changes of the pH value in some of our systems originate from the anomalous behaviour of the glass electrode (we have experienced that high  $\text{AgNO}_3$  concentrations make pH determination with glass electrodes erroneous), we carried out the determination of pH value of some HCl solutions and of some NaOH solutions containing various NaCl concentrations (from  $6 \times 10^{-1}N$  NaCl to  $0N$  NaCl). We found that the presence of NaCl did not influence the pH value determined by the glass electrode.

#### DISCUSSION

The behaviour of our four-component system: gelatin —  $\text{FeCl}_3$  — NaCl (neutral electrolyte) — pH is represented on Fig. 13. Starting from Fig. 13 as well as from other diagrams in more detailed form, we can survey the action of each parameter on the behaviour of our four-component system. This study will help to interpret these phenomena on the basis of the mutual action of simpler systems obtained by division of our four-component system.

A) *The action of each parameter on the behaviour of the four-component system: gelatin —  $\text{FeCl}_3$  — NaCl — pH*

A — 1) *The action of the  $\text{FeCl}_3$  concentration*

A — 1-a) *At high  $\text{FeCl}_3$  concentration the curve type A and C on Fig. 2. appears, represented as A and C also on Fig. 5. The maximum of the gel for-*

mation and the maximum of precipitated  $\text{Fe}(\text{OH})_3$  flocks are joined and the minimum between them disappears. The continuous increase of pH value changes the yellow colour of the gel into an orange one, after which the gel clumps and brown flocks appear together in the turbid liquid. At high pH value the brown flocks precipitate leaving a clear supernatant liquid.

A — 1-b) At the lower  $\text{FeCl}_3$  concentration a shallow minimum (»low turbidity«) appears (*D* on Figs. 2, 4 and 5). By the following decrease of  $\text{FeCl}_3$  concentration this minimum becomes deep (*E* on Figs. 2, 4 and 5) and separates the maximum of the gel formation from the maximum of brown  $\text{Fe}(\text{OH})_3$  flocks.

A — 1-c) The following decrease of  $\text{FeCl}_3$  concentration depresses the gel formation maximum which becomes lower and narrower (*H* on Figs. 3 and 5). Finally it disappears at *I* on Figs. 3 and 5. The maximum of brown  $\text{Fe}(\text{OH})_3$  flocks does not change.

A — 1-d) At the  $\text{FeCl}_3$  concentration approaching zero, that is at  $\log N \text{FeCl}_3 \rightarrow (-\infty)$ , the maximum of brown  $\text{Fe}(\text{OH})_3$  flocks disappears also.

#### A — 2) The action of pH value

A — 2-a) At the curve type *F* on Figs. 3 and 5 the pH value restricts the region of the gel formation maximum and of brown  $\text{Fe}(\text{OH})_3$  flocks maximum determining the limits of the minimum between them.

A — 2-b) At the curve type *A* on Figs. 2 and 5 the pH value restricts the acid side of the gel formation maximum, changes the feature of the gel and by continuous change results in the formation of brown  $\text{Fe}(\text{OH})_3$  flocks.

#### A — 3) The action of NaCl concentration

The influence of NaCl concentration can be seen on Fig. 13, comparing the diagrams on horizontal planes (Figs. 5, 12 II, III, IV, 14) and the diagrams joining them on the vertical planes (Figs. 9, 10, 11).

A — 3-a) By the increase of NaCl concentration the acid limit of the gel formation region is shifted towards lower pH values. This becomes evident by comparing the systems containing  $6 \times 10^{-1} N \text{NaCl}$  (Fig. 5) with the systems without NaCl (Fig. 14). At the lower  $\text{FeCl}_3$  concentrations the shift of the pH values is appreciable (Fig. 9), at the higher  $\text{FeCl}_3$  concentrations it is smaller or unnoticeable. (Figs. 10 and 11).

A — 3-b) The presence of a high NaCl concentration ( $6 \times 10^{-1} N$ ) makes the gel rigid and thixotropic, at a high  $\text{FeCl}_3$  concentration yellow and at a low  $\text{FeCl}_3$  concentration white (Fig. 5). After about a week the phenomenon of syneresis appears and the gel is similar to a dense compact clump with a separated clear liquid.

In general we may emphasize that at low  $\text{FeCl}_3$  concentrations an addition of NaCl into the system greatly influences the character of the gel. The higher the  $\text{FeCl}_3$  concentration, the lower the influence of NaCl separately added into the system.

If we consider the systems containing low  $\text{FeCl}_3$  concentrations, we notice that the lowering of NaCl concentration makes the gel less rigid. If the NaCl concentration decreases to zero (Fig. 14), the system loses its gel properties. Very large, frail, nearly transparent flocks appear swimming in the clear liquid (we call it »gel flock«).

A — 3-c) Fig. 14 represent the system without NaCl separately added into the system. We can see that the maximum of »gel formation« (in that case we have the mentioned »gel flock«) does not disappear when the  $\text{FeCl}_3$  concentration decreases to zero, i. e. when  $\log N \text{FeCl}_3 \rightarrow (-\infty)$ . In that case the system does not contain  $\text{FeCl}_3$ , and we have the isoelectric turbidity maximum of the system: gelatin — pH, which will be discussed in one of the following publications. That system is represented on the edge right down on Fig. 13. If we compare Fig. 14 with Fig. 5, we see that the presence of  $6 \times 10^{-1} N$  NaCl eliminates the gel formation maximum at I and at the lower  $\text{FeCl}_3$  concentrations, as well as the isoelectric turbidity maximum of the system: gelatin — pH, shown on Fig. 14.

B) *The method of investigation by division into simpler systems*

If we want to explain the phenomena occurring in our four-component system, we are obliged to study the mutual action of the components. It is therefore necessary to begin with the investigation of the simpler systems containing a lower number of components. By adding new components to the simpler systems or by compounding the simpler systems into a new one, we build the system with a greater number of components, and can finally build our four-component system. In such a complex system we have to find out the phenomena occurring in the simpler systems as well as the phenomena characteristic for that complex system. Such an analysis serves to find the character and mechanism of the occurring processes and their explanation.

In following publications we shall report on the investigations of the behaviour of the simpler systems:

$\text{FeCl}_3$  — pH,  
 $\text{FeCl}_3$  — NaCl — pH,  
 gelatin — pH,  
 gelatin — NaCl — pH,  
 gelatin —  $\text{FeCl}_3$  — pH,

from which our four-component system: gelatin —  $\text{FeCl}_3$  — NaCl — pH is composed.

In »General discussion and conclusions« we shall try to interpret our results.

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### IZVOD

**Vladanje sistema želatina — ferum(III) klorid — neutralni elektrolit — hidrogen klorid ili natrium hidroksid u vodenom mediju. I.  
Fenomenologija i način daljnjeg istraživanja dijeljenjem na jednostavnije sisteme**

R. Wolf i B. Težak

Istraživano je vladanje navedenog sistema, koji nazivamo: želatina —  $\text{FeCl}_3$  —  $\text{NaCl}$  (neutralni elektrolit) —  $\text{pH}$ . Na trodimenzionalnom dijagramu na sl. 13. prikazano je područje stvaranja gela, područje taloženja smeđih pahulja  $\text{Fe}(\text{OH})_3$ , područje, gdje gel i smeđe pahulje dolazi zajedno, kao i područje bistre otopine. Koncentracija želatine održavana je na konstantnoj vrijednosti 0.425%, ali su koncentracija  $\text{FeCl}_3$ , koncentracija  $\text{NaCl}$  i  $\text{pH}$  vrijednost varirale, te su njihove vrijednosti poslužile kao koordinate na sl. 13.

Slike 5, 9, 10, 11, 12 I, II, III, IV i 14 prikazuju sisteme, gdje je koncentracija jedne od komponenata održavana na konstantnoj vrijednosti, a prikazane su i na ravninama, koje presijecaju dijagram na sl. 13.

Promatrana je uloga pojedinih komponenata u vladanju četverokomponentnog sistema. U svrhu tumačenja tih pojava prikazan je način dijeljenja četverokomponentnog sistema u jednostavnije sisteme koje valja zasebno istražiti.

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