CCA-754

541.18.041:546.732
Conference Discussion

Interactions in the System: Gelatin—Sodium Chloride—Ferric Chloride—Hydrochloric Acid or Sodium Hydroxide*

R. H. H. Wolf

Laboratory of Physical Chemistry, Faculty of Science, University of Zagreb, and »Ruđer Bošković« Institute, 41000 Zagreb, Croatia, Yugoslavia

Received August 8, 1972

Colloidal states of the system: gelatin—NaCl—$FeCl_3$—HCl or NaOH (a strong gel, stable colloid, brown ferric hydroxide flocks) depend on the concentration of the components and pH. In order to establish the action of each component, the mentioned system was divided into simpler systems, the simpler systems were investigated separately, and conclusions regarding their interactions drawn.

The reaction of amphoteric polyelectrolyte gelatin, in the presence of NaCl, with ferric hydroxide in statu nascendi, was investigated in the system: gelatin--NaCl—$FeCl_3$—HCl or NaOH (prepared by mixing the aqueous $FeCl_3$ solution with a solution containing gelatin, NaCl and HCl or NaOH)[1,2]. The colloidal states of the system (a strong, thixotropic and very turbid pudding-like gel, a clear solution, and brown ferric hydroxide flocks) were the result of specific interactions between the components, and were dependent on the component concentrations and pH. Although the component concentrations and pH were established as parameters determining the colloidal state of the system[1,2], the question about the character of the interactions remained without an answer. The mentioned system: gelatin—NaCl——$FeCl_3$—HCl or NaOH was therefore divided into simpler systems with a lower number of components (Table I).

TABLE I

A) gelatin—NaCl—$FeCl_3$—HCl or NaOH [1,2]

↗ ↑ ↖

E) $FeCl_3$—NaCl—HCl or NaOH [6] | *F*) gelatin—NaCl—HCl or NaOH

↑ + NaCl | ↑ + NaCl

C) $FeCl_3$—HCl or NaOH [3] | *D*) gelatin—HCl or NaOH

↘ | + NaCl ↙

B) gelatin—$FeCl_3$—HCl or NaOH [5]

The simpler systems were investigated separately[3,5,6], their mutual actions studied[5], and an attempt was made to establish the influence of each component and the consequences of their interactions. The simpler system *C* contained — depending upon pH — soluble ferric species and colloidal ferric hydroxide (isoelectric point at pH 6.8[3]) in the form of brown flocks or a stable negatively charged colloid (the latter presented as »clear« at α—β—γ—δ in Fig. 1-C).

* Based on a discussion contribution presented at the *III International Summer School on the Chemistry of Solid/Liquid Interfaces,* Rovinj, Yugoslavia, July 1—5, 1972.

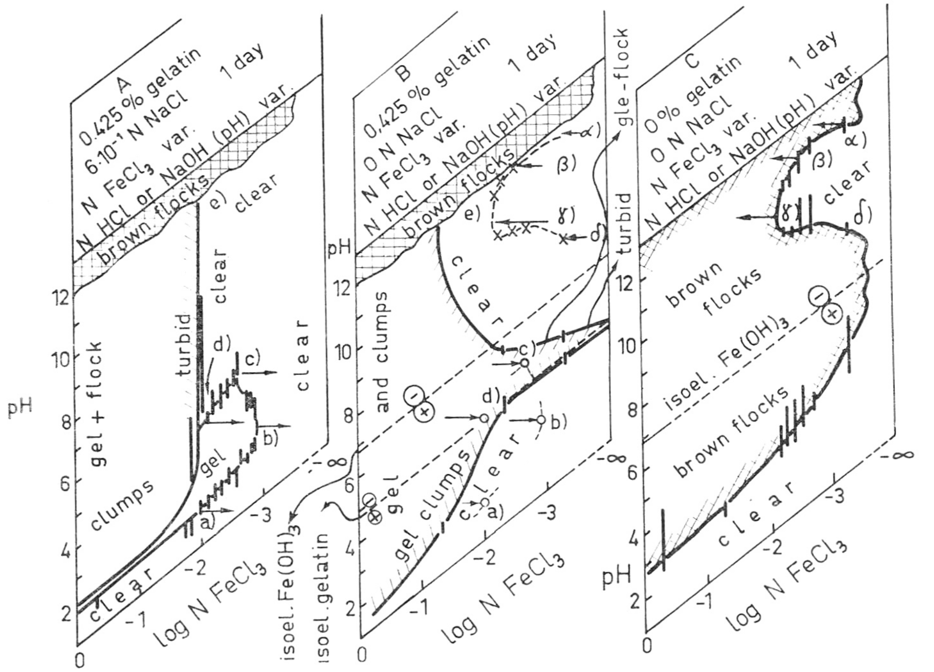

Fig. 1. (*A*): 0.425% gelatin — 6 · 10^{-1} *N* NaCl — *N* $FeCl_3$ varied — *N* HCl or NaOH varied; (*B*): 0.425% gelatin — *N* $FeCl_3$ varied — *N* HCl or NaOH varied; (*C*): *N* $FeCl_3$ varied — *N* HCl or NaOH varied. The colloidal state of the system (after 1 day) is given in dependence of *N* $FeCl_3$ (log scale) and *p*H. The limiting line α—β—γ—δ from C and a—b—c—d—e from A are projected to B for comparison.

The simpler system *D* contained gelatin molecules carrying positively and negatively charged groups. By increasing the pH, the number of positively charged groups per gelatin molecule diminished, the number of negatively charged groups increased, and their numbers were equal at the isoelectric point, pH 4.7. System *B*[5] was obtained by the fusion of systems *C* and *D* (Table I). Within the pH region limited by the isoelectric points of gelatin, pH 4.7, and of ferric hydroxide, pH 6.8, the ferric hydroxide was positively charged, and the gelatin molecules carried an excess of negatively charged groups. Near the equivalency of electric charges of opposite signs, a frail »gel-flock« (on the right-hand side in Fig. 1-B) was formed. The electrophoretically[4] determined relationship between the pH of zero charge of the »gel-flock« and the ratio between the gelatin and $FeCl_3$ concentrations indicated the adherence of gelatin groups to oppositely charged ferric hydroxide and/or reaction of gelatin with the ferric ion or complexes[5]. An excess of either a positive or a negative charge gave a stable colloid (»clear« in Fig. 1-B). The stabilizing action of gelatin is evident from the enlarged region of the stable system »clear« in Fig. 1-B (the limiting line α—β—γ—δ from Fig. 1-C is projected to Fig. 1-B for comparison). At pH higher than 12, no stabilization occured, and brown ferric hydroxide flocks were formed, evidently owing to the lack of positively charged groups of gelatin.

The influence of the NaCl component (6×10^{-1} *N*) on the simpler system *C* was different than the influence on the simpler system *D*. When added into system *C*, NaCl component coagulated the stable colloid in the α—β—γ—δ region in Fig. 1-C, and system *E* had brown ferric hydroxide flocks in the whole region from pH 3 to higher pH[6]. Regarding system *F*, the presence of NaCl made the gelatin molecules unfold[7,8], and the interacting power of gelatin was evidently enhanced. The action of the NaCl component in system *A* showed therefore two different effects: the enhancing of the interacting power of gelatin, on one hand ,and the coagulating action on ferric hydroxide, on the other hand. At a high ratio between the concentrations of gelatin and $FeCl_3$ components, the enhanced interacting power of gelatin predominated, causing the region of the stable system (»clear« on the right-hand side of a—b—c—d—e in Fig. 1-A), and of the strong, thixotropic and very turbid pudding-like gel in the region a—b—c—d at slightly lower values of the mentioned concentration ratio and appropriate pH region. By a further decrease of the mentioned concentration ratio, the coagulating action of NaCl appeared, and the stable region »clear« at d—e changed through »turbid« to the region where a mixture of gel with ferric hydroxide flocks (»gel+flock«) and clumps were formed (on the left-hand side of Fig. 1-A). Some results for the low concentration ratio, not presented here, have shown an extension of the region of brown ferric hydroxide flocks toward the lower pH. Regarding the agreement between systems *A* and *B* at extremely high $FeCl_3$ concentrations, it ought to be mentioned that system *B*, in these conditions, contained a high concentration of NaCl, not separately added into the system, but formed by reaction: $FeCl_3 + 3\,NaOH = 3\,NaCl + Fe(OH)_3$.

CONCLUSION

1. pH value (adjusted by the HCl or NaOH component) determines the concentrations of soluble ferric species and the charge of ferric hydroxide in system *C*, the numbers of positively and of negatively charged groups per gelatin molecule in system *D*, and the interacting relations in system *B*.

2. The ratio between the concentrations of gelatin and of $FeCl_3$ is a parameter, which — simultaneously with pH — determines the concentration relations between oppositely charged participants in the processes of interaction. Near the equivalency of opposite charges, the »gel-flock« is formed, while at the excess of a given charge the stable system (»clear«) is formed, as shown in system *B*.

3. The NaCl component on one hand enhances the interacting power of gelatin, and on the other hand has a coagulating action on colloidal ferric hydroxide. The NaCl component introduces therefore some particular relations in system *A*. A high value of the concentration ratio between gelatin and $FeCl_3$ makes the increased interacting power of gelatin predominate resulting in stabilization (»clear«) and the formation of a strong gel (a—b—c—d in Fig. 1-A). A lowering of the above mentioned concentration ratio makes the coagulating action predominate (appearance of brown flocks).

REFERENCES

1. R. Wolf and B. Težak, *Croat. Chem. Acta* **29** (1957) 461.
2. B. Težak, R. Wolf, and S. Kratohvil, *J. Chim. Phys.* **55** (1958) 307.
3. R. H. H. Wolf and B. Težak, *Croat. Chem. Acta* **33** (1961) 1.
4. M. E. Smith and M. W. Lisse, *J. Phys. Chem.* **40** (1936) 399.
5. R. H. H. Wolf and M. Vinceković, *Proceedings of the Vth International Congress of Surface Active Substances,* Barcelona 1968, Vol. II/2, 1113.
6. R. H. H. Wolf and B. Težak, *Croat. Chem. Acta* **33** (1961) 9.
7. G. Stainsby, *Nature* **169** (1952) 662.
8. H. Boedtker and P. Doty, *J. Phys. Chem.* **58** (1954) 968.

IZVOD

Uzajamno djelovanje komponenata u sistemu: želatina—NaCl—$FeCl_3$—HCl ili NaOH

R. H. H. Wolf

Koloidna stanja u sistemu: želatina—NaCl—$FeCl_3$—HCl ili NaOH (čvrsti gel, stabilni koloid, smeđe $Fe(OH)_3$ pahulje) zavise o koncentraciji komponenata i pH vrijednosti. U svrhu utvrđivanja djelovanja svake od komponenata, spomenuti je sistem bio razložen na jednostavnije sisteme, jednostavniji su sistemi bili zasebno ispitani, te stvoreni zaključci o njihovom uzajamnom djelovanju.

FIZIČKO-KEMIJSKI ZAVOD
PRIRODOSLOVNO-MATEMATIČKOG FAKULTETA
i
INSTITUT »RUĐER BOŠKOVIĆ«
41000 ZAGREB

Primljeno 8. kolovoza 1972.