

A Novel System Consisting of a Soluble Inorganic Reagent Caged in the Network Structure of Gels¹⁾

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A new type of system was prepared which consisted of a water-soluble macromolecular metal complex caged in the network structure of a gel particle, the caged reagent being soluble in nature in an aqueous solution, but unable to get out of the gel particle into the outside solution by going through the network because of its large molecular size. This system was further proved to be useful as a convenient capturer of heavy metal ions in an aqueous solution.

Since we found that gel chromatography using Sephadex was effective in separating the reaction products between the Cr(III) ion and the hexacyanoferrate(II) and succeeded in the isolation of pure $K_5CrFe_2(CN)_{12}$,²⁾ we have purified various metal complexes by utilizing this excellent ability of Sephadex gel to act as a molecular sieve. Therefore interested in the sieving function of the network structure of gel, we attempted to confine the water-soluble macromolecular metal complex in the network structure of a particle of gels. The desired soluble macromolecular metal complex reagent caged in the gel had to be produced from its components in any micropores in the network structure of a gel particle.

We first attempted to form a system consisting of soluble Prussian blue caged in the network structure of a gel such as Sephadex or agar.

The soluble Prussian blue, however, is in general not obtainable efficiently by the simple equimolar mixing of a solution of the iron(III) ion with that of the hexacyanoferrate(II) ion, but much of the precipitate of insoluble Prussian blue is formed in practice. This is because the procedure of such mixing does not allow the equimolecular reaction to take place predominantly in this case. Therefore we established a new process for preparing genuine soluble Prussian blue in a good yield by initiating the reaction in a semihomogeneous phase consisting of an equimolar mixture of the reactants.

By elevating the pH of an aqueous solution of iron(III) nitrate slowly to about 2.7, the Fe^{3+} ion in the solution can be transformed to a colloidal form of $Fe^{3+}(NO_3)_{3-x}(OH)_x$, which is unreactive to the $[Fe(CN)_6]^{4-}$ ion. The solution was thereafter mixed with the $K_4Fe(CN)_6$ solution to form a semihomogeneous phase containing Fe^{3+} and $Fe(CN)_6^{4-}$ in an approximately equimolar ratio. The reaction between the two reactants to form soluble Prussian blue was then initiated in the solution by acidifying the solution slowly to pH 2.4. This process proved to be a very excellent one for preparing soluble Prussian blue of a good quality in a good yield, giving a composition of approximately 1:2:6 for the molar ratio of K:Fe:CN and a yield of above 74% for the product after purification by the use of the Sephadex G-50 column, followed by evaporation to dryness.

Thus, our desired systems of caged Prussian blue were prepared by causing the above-described new process to take place within the network structure

of Sephadex and agar gels swollen in an aqueous solution, thus producing the soluble Prussian blue there.

The fact that the soluble Prussian blue was caged in the network structure of those gels was shown by means of microscopic and electron-microscopic photographs of the systems. The reagent caged in the structure further proved to have the original nature of soluble Prussian blue in its color, composition, and reactivity with certain metal ions, such as Fe^{3+} , Cr^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , and Zn^{2+} .

The reactivity maintained on the caged Prussian blue confirmed our expectation that the system would be an excellent capturer of heavy metal ions in an aqueous solution. It was experimentally ascertained that the heavy metal ions could be easily removed from a solution by a simple procedure consisting of putting the system into a solution and by then removing it after stirring.

Experimental and Results

Eight grams of Sephadex or agar were made to swell in 200 cm³ of an aqueous solution containing 0.01 mol of iron(III) nitrate. To the mixture we then added 0.025 mol of potassium hydrogencarbonate dissolved in 20 cm³ of water, so that the iron(III) ion inside as well as outside gel particles was transformed into unreactive colloidal iron(III) nitrate hydroxide.³⁾ The resulting mixture was slowly poured into 200 cm³ of an aqueous solution containing 0.01 mol of potassium hexacyanoferrate(II), and after the continued stirring the new mixture was allowed to stand overnight. The mixture was then slowly acidified to pH 2.4 with 1 mol dm⁻³ nitric acid to make the already-mixed components start the reaction to form the soluble Prussian blue. The mixture was filtered, and the soluble Prussian blue outside the structure of the gel was washed off with water until the filtrate

TABLE 1. ANALYTICAL RESULTS OF THE SOLUBLE PRUSSIAN BLUE IN THE SYSTEM

		K	Fe	CN	K : Fe : CN
		(10 ⁻⁴ g-ion/1 g-gel)			(molar ratio)
Sephadex gel	G-10	0.27	0.76	1.6	0.71 : 2 : 4.2
	G-15	0.63	1.50	4.1	0.84 : 2 : 5.5
	G-25	1.31	3.84	10.2	0.68 : 2 : 5.31
	G-50	1.91	5.91	17.1	0.64 : 2 : 5.79
	G-75	2.45	7.05	19.7	0.70 : 2 : 5.59
	G-150	2.09	6.79	19.7	0.62 : 2 : 5.80
Agar gel		4.04	9.95	30.7	0.81 : 2 : 6.17
Molar ratio of K, Fe, CN in soluble Prussian blue, calculated as $KFe_2(CN)_6$					1 : 2 : 6

TABLE 2. ION-EXCHANGE CAPACITY OF SOLUBLE PRUSSIAN BLUE CAGED IN THE GEL FOR METAL IONS (BATCH OPERATION)
(unit: 10^{-4} g-ion dm^{-3})

Metal ions ^{a)}		Fe ³⁺	Cr ³⁺	Co ²⁺	Ni ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺	Mn ²⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺	Pb ²⁺
Original concentration of metal ions		{ 2.0 (3.2)	{ 2.0 (3.8)	{ 3.0 (5.3)	{ 3.0 (5.9)	{ 3.0 (6.0)	{ 3.0 (5.6)	{ 3.0 (5.8)	{ 3.0 (6.0)	{ 3.0 (5.1)	{ 3.0 (5.6)	{ 3.0 (5.6)	{ 3.0 (4.9)
Equilibrium concentration of metal ions in the presence of the gels examined	Sephadex G-75 gel	{ Gel only { 1.0 (5.2)	{ 1.6 (5.4)	{ 2.1 (6.7)	{ 2.8 (6.6)	{ 2.4 (7.7)	{ 2.7 (7.8)	{ 1.8 (6.7)	{ 2.6 (7.7)	{ 2.4 (6.1)	{ 2.2 (6.5)	{ 2.4 (6.7)	{ 2.1 (6.1)
		{ Gel containing P.b. { 0.3 (3.3)	{ 0.2 (3.4)	{ 0.3 (3.5)	{ 0.1 (3.4)	{ 0.6 (4.2)	{ 0.9 (4.2)	{ 0.7 (4.2)	{ 0.5 (3.8)	{ 0.1 (3.3)	{ 0.1 (3.4)	{ 0.1 (3.5)	{ 0.4 (4.0)
	Agar gel	{ Gel only { 1.8 (5.5)	{ 0.5 (6.2)	{ 0.8 (6.8)	{ 0.9 (6.9)	{ 2.4 (7.4)	{ 0.3 (7.3)	{ 0.7 (7.0)	{ 0.8 (7.1)	{ 0.4 (6.1)	{ 0.5 (6.8)	{ 0.3 (6.7)	{ 0.1 (5.8)
		{ Gel containing P.b. { 1.8 ^{b)} (3.3)	{ 0.0 (3.4)	{ 0.0 (3.6)	{ 0.0 (3.6)	{ 0.3 (3.7)	{ 0.0 (3.6)	{ 0.0 (3.7)	{ 0.0 (3.6)	{ 0.0 (3.4)	{ 0.0 (3.5)	{ 0.0 (3.6)	{ 0.0 (3.6)

a) Test solutions of the individual metal ions were prepared from their nitrate salts and were used in the test without the addition of any buffer agent. The figures in the parentheses beneath the analytical results indicate the pH values of the intact sample solution and the equilibrium solutions in each case. b) In this case, the Fe³⁺ ion in the red-colored sample solution was considered to have been partially hydrolysed and to exist as the colloidal state iron(III) nitrate hydroxide, it might be unable to diffuse into gel particles.

was no longer blue. The resulting blue particles of gel were preserved in water or dried.

The analytical results on the soluble Prussian blue in the system prepared are shown in Table 1. The high level of potassium content is considered to be proof of the fact that the majority of the blue is soluble Prussian blue. Under the conditions used in this work to prepare the system, among a variety of Sephadex gels (G-10, 15, 25, 50, 75, and 150) G-75 gel was the most suitable as a material for the preparation.

A microscopic photograph of the frozen slice of the Sephadex G-75 gel containing the soluble Prussian blue is shown in Fig. 1, from which it can be found that Prussian blue is well prepared in the network structure of gel. From the electron-microscopic photograph shown in Fig. 2, it is found that the Prussian blue is preserved as particles of 5 to 50 nm in size in the gel particle. In view of the fact that soluble Prussian blue is non-adsorptive to Sephadex gel,⁴⁾ these two photographs demonstrate that the soluble Prussian blue is caged in the gel particle.

When the system was swollen in water, a batch of it vividly captured various heavy metal ions. Tests of the ability of this system to capture the heavy metal ions in an aqueous solution in the batch procedure were carried out by using 0.1 g of each dry gel and 5 cm³ of a solution containing

the metal ions in the concentrations shown in Table 2. After having been allowed to stand overnight, the supernatants were taken for chemical analyses. The analytical results revealed a strong activity of the system in capturing heavy metal ions (Table 2).

Discussion

Our original expectation that a very soluble reagent of a large molecular size could be caged in the network structure of gel, and that it could be confined in the gel particle, was successfully realized in the preparation of this system.

On such a novel system in which intact soluble Prussian blue is caged, it had been further expected that the system would be an excellent capturer of heavy metal ions in an aqueous solution, since soluble Prussian blue reacts with ions of various heavy metals to form precipitates. The heavy metal ion in the solution would be able to diffuse into the gel particle through the network structure in the gel particle, and would then collide with the molecule of soluble Prussian blue residing there and react with the blue to be trapped. Thus, the heavy metal ion would not be able to return to the outside solution. This expectation as to the system was materialized, also, by the observation of its ability as a heavy-metal-ion capturer.

Recently, a way of combining two polymers to form such systems called "interpenetrating polymer network systems", has come to attract chemists' interest as a third possible way of combining two different types of polymers for the purpose of modifying the properties of individual polymers,⁵⁾ coming to supplement the conventional mechanical blending and copolymerization. This third way has, however, been used mostly to combine the elastomer-type polymer and the glassy-type polymer.

In the present work we accomplished the preparation of a new art of macromolecular system, in which the water soluble macromolecular electrolyte of an inorganic metal complex was confined within the swollen gel. The intriguing features of the structure and

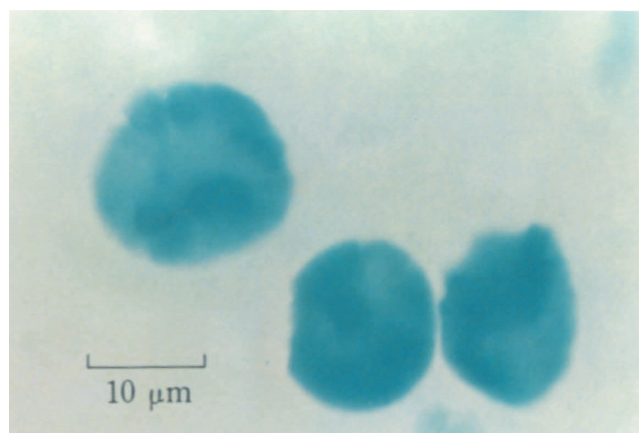


Fig. 1. Microscopic photograph of the frozen slice of the Sephadex G-75 gel particles in which the soluble Prussian blue is caged.

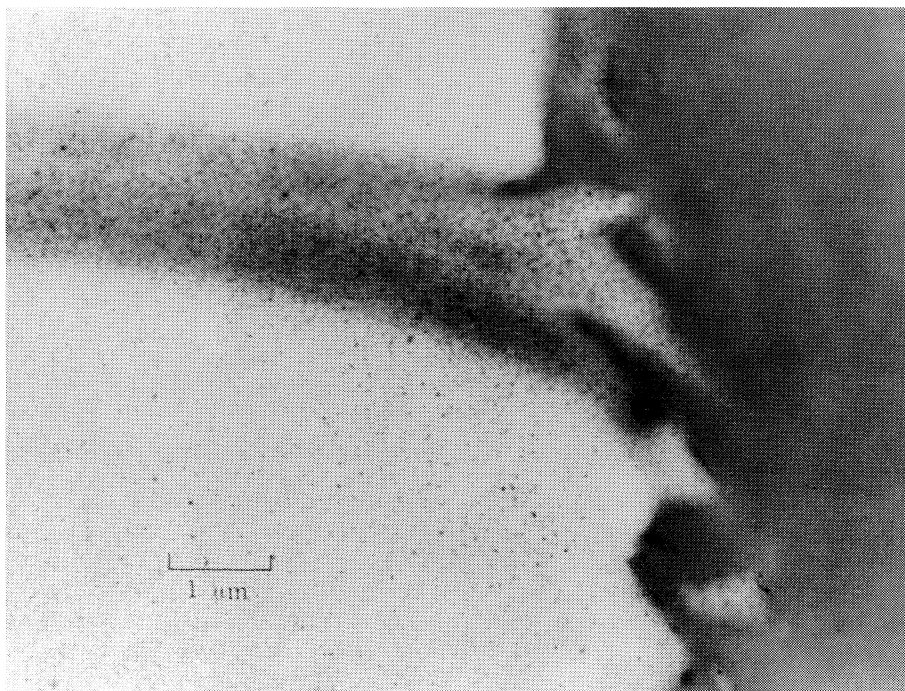


Fig. 2. Electron-microscopic photograph of soluble Prussian blue caged in the Sephadex G-75 gel. The sample system was embedded in Epon 812 after dehydrated with Durcupan.

nature, as well as the practical utility of the system, were also experimentally ascertained in this work.

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