THE SOL-GEL TRANSFORMATION IN GELATIN

By DAVID M. GREENBERG and M. A. MACKEY

(*From the Division of Biochemistry, University of California Medical School, Berkeley*)

In recent years there has been a revival of interest in the micellar theory of structure proposed by Nägeli in 1852 as a theory for the structure of protoplasm. This theory has been taken over by colloid chemists and applied to the structure of many colloids as a result of the work of Zsigmondy (1), Pauli (2), McBain (3, 4) and their co-workers. Laing and McBain (4) have further extended the micellar theory to the sol-gel transformation by proposing that the micellar unit of the gel state is identical with that in the sol. According to these authors: "All that is necessary is to assume that the particles become stuck together or oriented into loose aggregates, which may be chance granules or, more probably threads." This conception is based on a study of sodium oleate, for which they found that in spite of the enormous change in viscosity involved in the change from sol to gel, such properties as electrical conductivity, lowering of the vapor pressure, refractive index, and sodium ion concentration remained identical in both the sol and the gel state. In support of their theory, Laing and McBain point out that Arrhenius (5) found the conductivity in gelatin-water-salt systems to be the same in both sol and gel. This aspect of the micellar theory has been extended by Gelfan (6) to protoplasm because he found that the conductivity of protoplasm remained independent of changes in viscosity and by Gelfan and Quigley (7) to the blood coagulation process since their experiments showed that during the coagulation process there is no change in the conductivity of shed whole blood or plasma, in spite of the almost infinite increase in viscosity during coagulation.

In view of the concentration of excess electrolytes in the gelatin experiments of Arrhenius, as well as in protoplasm and in blood, the question arises whether the generalization from the findings on sodium

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oleate to all gelling systems, particularly among the proteins, is valid. In other words, is the identity of conductivity in the sol and gel state due to an identical micellar structure of these protein systems, or is it due to the conductivity of the excess electrolytes being so much greater than the conductivity of the ionized protein salts that the difference in conductivity produced by the structural changes involved in the sol-gel transformation was not detectable by the experimental procedure employed? That there is little or no change in the conductivity and diffusibility of electrolytes in colloidal systems on changing from sol to gel has long been known and is not a vital point in connection with the micellar theory of Laing and McBain, since all theories of gel structure postulate that the structure produced is enormous in size compared with ionic dimensions and thus exerts almost no hindering effect on ionic movement.

To obtain a fuller insight into the question, the following study has been carried out on the conductivity of gelatin sols and gels. Gelatin was selected because it is an example of a protein capable of undergoing a reversible sol-gel transformation. In carrying out the study we had in mind the work of Krishnamurti (8) who, from a study of the light-scattering in sols and gels of agar, has concluded that the micellar structures in the two states are not identical; and also that of Craig and Schmidt (9) who found differences between the refractive indices of gelatin sols and gels.

Experimental Procedure

In measuring the conductivity, the Kohlrausch principle was employed, with the difference that a one-stage vacuum tube amplifier was introduced between the bridge and the telephone, which made it readily possible to make measurements accurate to 0.1 per cent. The source of the bridge current was a General Radio Oscillator, and the capacity of the conducting cell was balanced in parallel by the setting of an adjustable condensor. The conductivity cell used throughout the experiments was of the bottle type, constructed of Pyrex glass. A thermometer, readable to 0.1°, was fitted into the neck of the cell in such a way that it could be immersed in the gelatin without interfering with the continuity of the liquid betweeen the electrodes. All measurements were made at 25°C. "Difco" granular gelatin was used in the experiments. It was purified and made ash-free according to the procedure described by Loeb (10). The purified gelatin on analysis was found to be totally ash-free and in aqueous solutions to have a pH value of 4.75 as measured by the hydrogen electrode. The analysis of the gelatin

in the experimental solutions was carried out by evaporating 10 cc. portions to dryness in porcelain crucibles and then heating at 110°C. to constant weight.

The plan of the experiments was to warm the gelatin to a temperature of about 37° to obtain the sol, fill the conductivity cell with the liquid gelatin, and then immerse the filled cell in an oil thermostat kept at 25°. The leads of the conductivity bridge were connected with the cell and when the temperature of the gelatin fell to 25° as shown by the thermometer immersed in the gelatin, the conductivity reading was first taken, and then further readings were made at various time intervals. To check the conductivity readings, the gelatin in the cell was again warmed up to 37° and the procedure repeated. To obtain the conductivity of the gel, the cell filled with gelatin was cooled down in an ice chest to about 10° to obtain a firm gel. The conductivity cell was then returned to the 25° bath and the conductivity reading taken when the gel reached the 25° temperature. As with the sol, the readings for the gel were checked by repeating the cooling.

RESULTS

The experiments carried out were first, a series at different concentrations of the pure isoelectric gelatin itself to determine the effect of variation in the concentration of gelatin. The results of this series are given in Table I. In this series, it was found that all concentrations of gelatin above 1 per cent set to a firm gel at 25°, but that concentrations of 1 per cent or less remained in a semiliquid state at this temperature. From the results on the pure gelatin, a concentration of gelatin was selected that would set to a firm gel at the temperature of the conductivity measurements, namely, about 3 per cent, and experiments were next carried out on the effects of electrolytes on the conductivity of the sol-gel transformation. The electrolytes used were hydrochloric acid, sodium hydroxide, and sodium chloride at varying concentrations. The results of these experiments are recorded in Table II where there are recorded the gelatin content, the concentration of electrolyte added, the conductivity of sol and gel respectively, and the percentage difference of conductivity between the two states.

In the measurement of the conductivity of the gelatin sols and gels it was found, except for those samples where there was no difference in conductivity between sol and gel, that the conductivity did not attain a constant value as soon as the 25° temperature was attained, but on the contrary, continued to drift slowly even though the temperature remained unchanged thereafter. This drift was in the direction of a

decreasing conductivity for the sol and an increasing conductivity for the gel, which on being allowed sufficient time, starting from either

TABLE I

The Conductivity of Ash-Free Gelatin Sols and Gels

Gelatin	Sol specific conductivity mhos $\times 10^5$	Gel specific conductivity mhos $\times 10^5$	Difference	Remarks
per cent			*per cent*	
0.90	4.27	4.27	0	Sol stable at 25°
1.67	6.70	6.49	3.1	Gel stable form
2.17	7.21	7.05	3.2	Gel stable form
2.62	8.70	8.28	4.8	Gel stable form
4.58	13.60	12.68	6.7	Gel stable form

TABLE II

The Influence of Electrolytes on the Conductivity of Gelatin Sols and Gels*

Electrolyte	Concentration N	Gelatin	Sol specific conductivity mhos $\times 10^5$	Gel specific conductivity mhos $\times 10^5$	Difference
		per cent			*per cent*
0	0	2.80	9.98	8.96	10.2
HCl	1.25×10^{-4}	2.80	11.32	10.14	10.0
HCl	1.24×10^{-3}	2.75	19.10	18.65	2.3
HCl	1.14×10^{-2}	2.55	99.70	99.70	0
0	0	2.70	9.44	9.73	7.6
NaOH	9.79×10^{-5}	2.70	10.00	9.90	4.1
NaOH	9.70×10^{-4}	2.65	15.55	15.00	3.8
NaOH	8.90×10^{-3}	2.45	53.25	53.25	0
0	0	2.90	9.81	8.82	10.1
NaCl	8.85×10^{-5}	2.90	12.50	12.10	3.4
NaCl	8.77×10^{-4}	2.90	22.15	21.75	1.9
NaCl	8.05×10^{-3}	2.65	98.35	97.90	0.4

* The lack of correspondence to a small degree between the gelatin concentration and the conductivity in certain of the experiments listed is explained by the drift in the conductivity noted in the text which makes an exact reproducibility in gelatin solutions impossible.

the sol or gel state, finally reached a constant value representative of the equilibrium state of the gelatin at that temperature. In the

present experiments, this equilibrium state for all except the 0.9 per cent gelatin of Table I was a firm gel. In the experiments where no difference in conductivity was found between the sol and gel condition, this drift was absent and in these samples when the thermostat temperature was once attained, the conductivity became constant. This was the result found for the first experiment of Table I, with a concentration of 0.90 per cent gelatin for which a semiliquid state was the state at 25° and for the experiments of Table II where the conductivity difference between sol and gel was zero although firm gels were stable at the 25° temperature. The conductivity figures for the rest of the experiments in Tables I and II are the values measured just after the thermostat temperature was attained by the gelatin.

The data with the pure gelatin and the electrolyte-containing gelatin solutions are not in accord with McBain's theory. Rather they are in harmony with the viewpoint that there is a distinct difference in the micellar units of the sol and gel state when a definite firm gel is formed. The gel state shows the lower conductivity of the two forms, which would be expected if the micellar unit of the gel is composed of aggregates of the sol micelles, thus naturally resulting in a lower electrical mobility. That the difference in conductivity is due mainly to electrical changes accompanying the structural changes of the sol-gel transformation is indicated by the experiments of Table I. Since in these experiments, the gelatin was completely ash-free, the measured conductivity can only be a measure of the electrical charge of the gelatin in the solution and the accompanying hydrogen ions. From the pH value of 4.75 given by these solutions, the hydrogen ion concentration is less than 2×10^{-5} mols per liter, which, using the value of 350 for the hydrogen ion mobility, leads to the value of 0.7×10^{-5} for the specific conductivity. This value in comparison with the values found for the gelatin, points to the conductivity coming mainly from the charged gelatin and that the decrease in conductivity on gelation is due to aggregation of the gelatin units.

The data of Table II substantiate this point of view. When the electrolyte concentration is low there is a distinct difference between the conductivity of the sol and gel state. This difference decreases with increase in the electrolyte concentration and is no longer detected when the conductivity of the electrolyte-containing solutions increases

to about 100-fold the value of the difference in the conductivity between the sol and gel of the original isoelectric gelatin.

The conductivity difference between the gelatin sols and gels as shown in Table II becomes undetectable at an electrolyte concentration of approximately 0.01 molal, yet blood and protoplasm contain more than tenfold this amount. On this account, the experiments on the electrolyte-containing gelatin solutions throw grave doubts on the conclusion drawn by Gelfan for protoplasm and by Gelfan and Quigley for the blood coagulation process. In view of the large excess of free electrolytes in the systems studied by the above authors, the fact that they found no change in conductivity with changes in viscosity or on gelation, is, under the circumstances, no proof of either an identity of micellar structure in the different physical states of the systems they studied or of a micellar structure at all.

From the present studies, along with Craig and Schmidt's refractometric results, and the work of Krishnamurti on agar, it must be concluded that the McBain theory of an identical unit structure for the sol-gel state has no general applicability.

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