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The effect of electrolytes on rigidity and diffusion in gelatin–glycerin gels

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The effect of electrolytes on the rigidity of and diffusion of dye from gelatin–glycerin gels has been examined. Cations, which might be expected to reduce the rigidity in the ratio of their valency, produced a fall in rigidity in the ratio Na^+, 1 : Ca^{++}, 1·25 : Al^{+++}, 1·57. This approximate halving of the effect is attributed to interference by the chloride ion. The rigidity was proportional to the square root of the ionic concentration except with sodium ferrocyanide where no simple relation held. A simple expression $G = G_0 (1 \pm \sqrt{I})$ was found for the rigidity, the sign depending whether anion or cation was considered. The effect of anions and cations on diffusion was as varied as their effect on rigidity. The addition of chlorides increased the diffusion coefficient in the order Al > Ca > Na. Both multivalent anions examined produced a decrease in diffusion coefficient; the sulphate being less effective than the ferrocyanide.

ELECTROLYTES have long been known to affect the rigidity of gelatin gels, even in the small amounts found in the ash of commercial material. Northrop & Kunitz (1926) and Bungenberg de Jong & Henneman (1932) reported a general lowering of rigidity at low concentrations of gelatin, whilst Narayanamurti & Gupta (1958) found the reverse. Cumper & Alexander (1952) found the rigidity to be decreased proportionately to the square root of the ionic strength.

Previously, Nixon, Georgakopoulos & Carless (1966, 1967) investigated factors controlling the rigidity and diffusion from gelatin–glycerin gels. This work has been extended to the effect of added electrolyte on rigidity and diffusion.

Experimental

MATERIALS

Gelatins. The characteristics have been given by Nixon & others (1966). *Glycerin* was Analar grade and *methylene blue* was of B.P. quality. *Electrolytes* were Analar grade and the *purified water* was once distilled from an all glass still (pH 5·2, specific conductivity 5 mhos cm^{-1}).

METHODS

The preparation of the gels, measurement of rigidity and the method of measuring the diffusion coefficient were as reported by Nixon & others (1966, 1967).

Results and discussion

The rigidity of gelatin–glycerin gels containing sodium chloride, calcium chloride, aluminium chloride, sodium sulphate and sodium ferrocyanide has been examined.

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An increase in the cation concentration caused a decrease in the rigidity of the gels at the gelatin–glycerin ratios studied (Figs 1 and 2). The rigidity could be expressed by the equation

$$G = G_0 (1 - K \sqrt{I}) \quad .. \quad .. \quad .. \quad 1$$

where G_0 = rigidity in absence of electrolyte; I = ionic strength; K = constant (slope /G_0). This type of relation is similar to that reported by Cumper & Alexander (1952) but the numerical values of the constants are much smaller because of the effect of glycerin on the rigidity which is

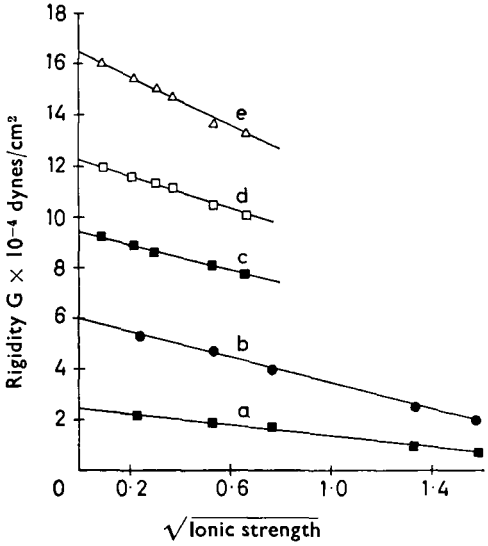


FIG. 1. Rigidity modulus as a function of the square root of the ionic strength of electrolyte. Gelatin Bloom strength: ● 99, ■ 154, □ 200, △ 250. % w/w gelatin–glycerin ratios: (a) = 5:20, (b, c, d, e) = 15:20. Electrolyte (a, b) = $AlCl_3$, (c, d, e) = NaCl. Temp. 25° ± 0·1°. Method of measurement: "Rigidometer".

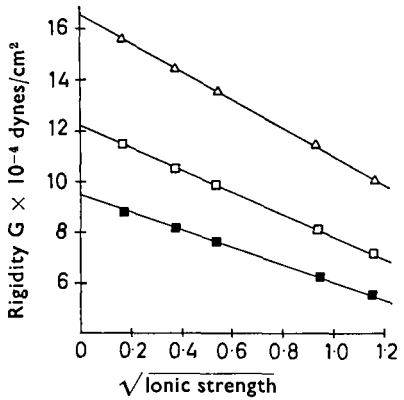


FIG. 2. Rigidity modulus as a function of the square root of the ionic strength of calcium chloride. Gelatin Bloom strength: ■ 154, □ 200, △ 250. % w/w gelatin–glycerin ratio: 15:20. Temp. 25° ± 0·1°. Method of measurement: "Rigidometer".

increased without a corresponding increase in the number of interchain linkages (Nixon & others, 1966). It was also observed that the addition of aluminium chloride caused shrinkage of the gels and that gelatin gels prepared from low Bloom number material exhibited viscoelastic properties (Fig. 3).

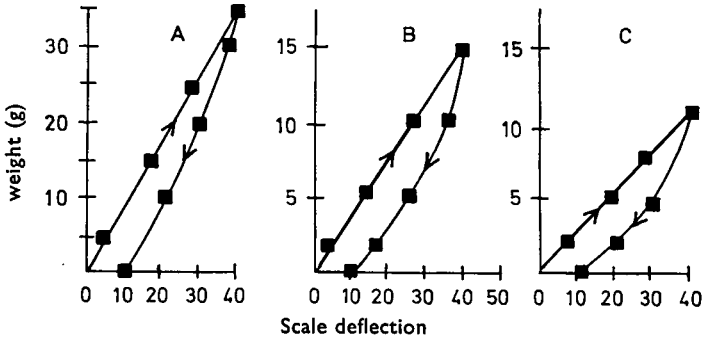


FIG. 3. Plastic behaviour of gelatin–glycerin gels in the presence of aluminium chloride. Gelatin Bloom strength: 154. % w/w gelatin–glycerin ratio: 10:20. $AlCl_3$: (A) 0·01M, (B) 0·15M, (C) 0·4M. Temp. 25° ± 0·1°. Method of measurement: "F.I.R.A. gel tester".

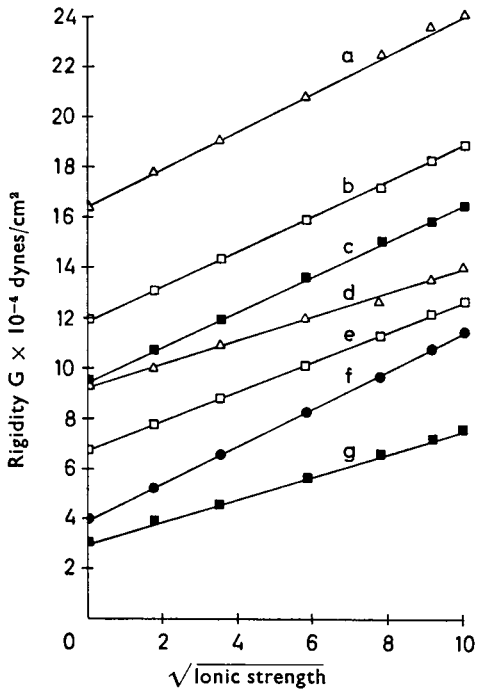
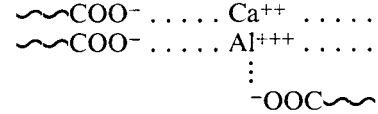


FIG. 4. Rigidity modulus as a function of the square root of the ionic strength of sodium sulphate. Gelatin Bloom strength: ● 99, ■ 154, □ 200, △ 250. % w/w gelatin–glycerin ratio: (a, b, c, f) = 15:20, (d, e, g) = 10:20. Temp. 25° ± 0·1°. Method of measurement: "Rigidometer".

The effect of cation valency on rigidity may be modified by the tendency of the chloride anion to reduce the rigidity by peptizing the gel linkages. The relative decrease produced by equimolar salt concentrations in gels with the same gelatin–glycerin ratio was approximately constant, but the absolute decrease was more pronounced with the chlorides of higher valency.

The metal cation opposed the reduction in rigidity produced by the chloride ion. Calcium and aluminium ions act through salt bridges to increase the number of gel linkages and thus produce a more rigid structure:



Because sodium is monovalent the sum total effect is that of the chloride ion. Using equation 1 it was possible to calculate the relative fall in rigidity produced by equi-ionic concentrations of the three salts.

	NaCl :	$CaCl_2$:	$AlCl_3$
Calculated ..	1 :	1·25 :	1·57
Expected ..	1 :	2 :	3

It will be seen that the overall effect of the calcium and aluminium salts

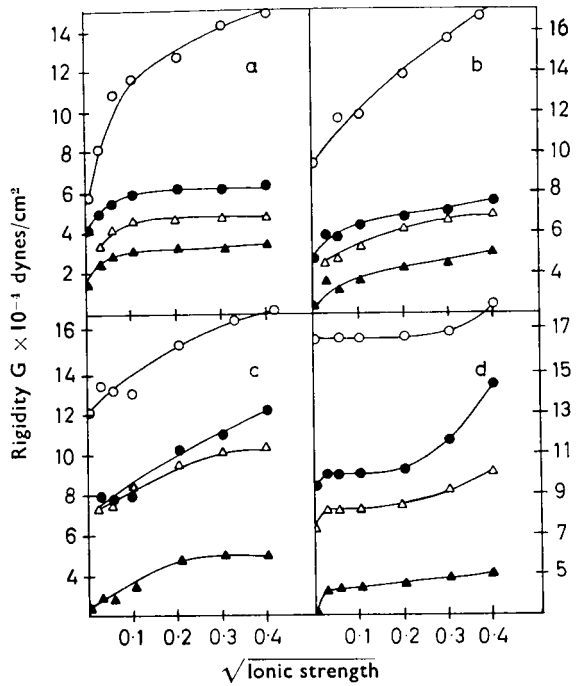


FIG. 5. Rigidity modulus as a function of the square root of the ionic strength of sodium ferrocyanide. Gelatin Bloom strength (a) 99, (b) 154, (c) 200, (d) 250. % w/w gelatin–glycerin ratio: ○ 15:20, ● 10:20, △ 8:20, ▲ 5:20. Temp. 25° ± 0·1°. Method of measurement: "Rigidometer".

is only approximately half that expected from their valency, indicating clearly the opposing effects of the anion and cation.

In contrast to the decrease in rigidity found with sodium chloride, the presence of multivalent anions such as sulphate and ferrocyanide produced an increase in rigidity (Figs 4 and 5). This increase was relatively greatest at low anion concentrations whilst at high concentration of gelatin the gel produced was almost rigid. A simple linear relation was found for sulphate ion, the only difference from equation 1 being a change of sign.

$$G = G_0 (1 + K \sqrt{SO_4^{--}}) \quad .. \quad .. \quad .. \quad 2$$

No such simple relation could be established for sodium ferrocyanide. Whilst the rigidity increased steeply with increasing low concentrations of ferrocyanide a constant value was approached at higher concentrations (Fig. 5a–c). The concentration of gelatin affected the behaviour of the system to this anion. With gelatins of up to 200 Bloom jelly strength, the increase in rigidity the anion produced with 15% gelatin gels was far more pronounced than that at lower gelatin concentrations. The 250 Bloom gelatin showed a completely different ferrocyanide effect. With these gels a concentration of up to 0·2M ferrocyanide produced only a slight increase in rigidity, but at anion concentrations above this the rigidity increased steeply (Fig. 5d).

Because of the non-interference of the monovalent sodium ion the increased rigidity produced by sodium sulphate and ferrocyanide must be caused by the multivalent anion. As with the multivalent cations calcium

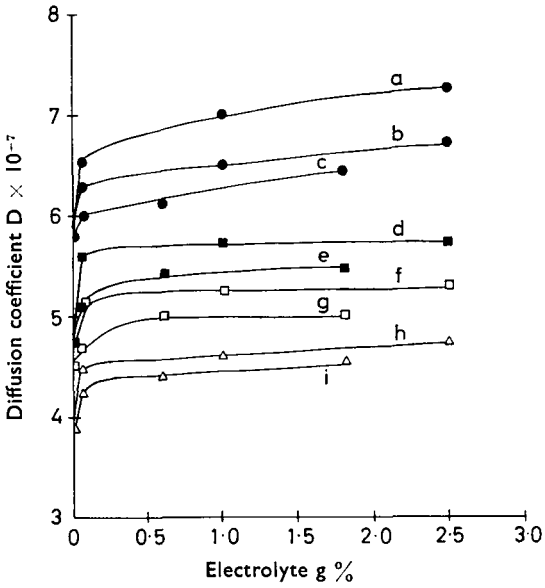


FIG. 6. The effect of anion concentration on the diffusion coefficient of methylene blue from gelatin–glycerin gels. Gelatin Bloom strength: ● 99, ■ 154, □ 200, △ 250. % w/w gelatin–glycerin ratio 10:20. Methylene blue 9·5 mg %. Electrolyte: (a) $AlCl_3$, (b, d, f, h) $CaCl_2$, (c, e, g, i) NaCl. Temp. 25° ± 0·1°.

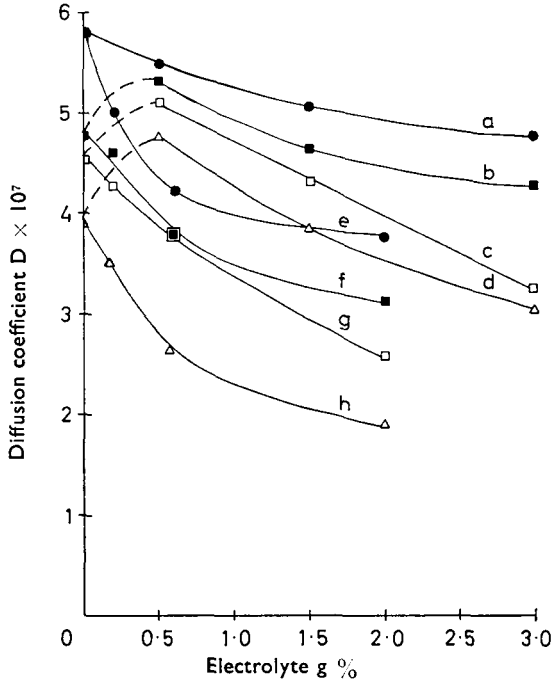


FIG. 7. The effect of cation concentration on the diffusion coefficient of methylene blue from gelatin–glycerin gels. Gelatin Bloom strength: ● 99, ■ 154, □ 200, △ 250. % w/w gelatin–glycerin ratio: 10:20. Methylene blue 9·5 mg %. Electrolyte: (a, b, c, d) Na_2SO_4; (e, f, g, h) $Na_4[Fe(CN)_6]$. Temp. 25° ± 0·1°.

or aluminium, these anions can form salt bridges between the gelatin chains and thus increase the rigidity.

These salt linkages are non-directional and therefore the existence of a bond does not necessarily imply that it will contribute to the shear rigidity. Only those bonds opposing the chain in the particular direction in which the force was applied would be effective.

The difference in the effect of cations and anions on the diffusion of methylene blue from the gels (Figs 6 and 7) was as sharp as that on the rigidity. The addition of the chlorides increased the diffusion coefficient in the order $AlCl_3 > CaCl_2 > NaCl$. The multivalent anions produced a decrease in diffusion coefficient, the sulphate being less effective than the ferrocyanide. Whilst the effect of the electrolytes was more pronounced with high Bloom number gelatins, no simple relation could be derived for diffusion coefficient and either salt concentrations or ionic strength.

The change in diffusion rate can be linked with changes in the gel microstructure. The chlorides increase the pore size by peptizing certain of the gel linkages and allowing fewer points of contact along the gelatin chain. Conversely the pore size of gels will tend to be decreased by the presence of calcium and aluminium ions. It is the overall balance between these two conflicting factors which results in the decrease in rigidity

accompanied by an increased pore size, and consequently an increased diffusion coefficient. The multivalent cations decrease the pore size by providing additional linkages between adjacent chains so that not only does the rigidity increase but the diffusion coefficient falls. The gelatins of high Bloom strength exhibited these effects in the most pronounced form because the long-chain length materials present allow more linkages per molecular unit.

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