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On the nature of the maximum gelation temperature in polymer gels

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Abstract

A theoretical framework is provided to explain the maximum gelation temperature in thermoreversible gelatin gels. Arrenhius plots of the inverse of the induction time of gelation versus the reciprocal of the setting temperature were linear for the different initial sol concentrations studied. Moreover, when extrapolated to higher temperatures, these lines intersected at a critical temperature. In this work, we show how this critical temperature corresponds to the temperature at which the polymer sol is in equilibrium with its activated state for a gelation reaction. We define this critical temperature as the maximum gelation temperature.

Keywords: Polymer gels; Gelation; Gelation temperature; Kinetics; Thermodynamics

1. Introduction

In a previous report [1], we proposed new ways of determining and defining the maximum gelation temperature of gelatin, a thermoreversible polymer gel. In that work, we observed that log–log plots of the induction time of gelation (t_{gel}) versus the setting temperature were linear for the different initial polymer concentrations. Moreover, the lines intersected at a particular temperature, which we defined as the maximum gelation temperature (T_{gel}). This experimentally determined maximum gelation temperature was very close to the theta temperature of the polymer–solvent system, the maximum theoretical temperature where gelation could take place. In this work, we provide a theoretical framework to explain why the intersection point of the above-mentioned new method should correspond to the theta temperature, the maximum temperature at which a polymer solution can gel.

2. Theory

The rate of a chemical reaction is proportional to the initial concentration of reacting species (c) raised to a power (x), which equals the order of that reaction, namely:

$$\mathrm{rate} = kc^{x} \tag{1}$$

where k is the rate constant for the particular reaction. The rate of a gelation reaction can be approximated by the inverse of the critical gelation time (τ_{c}) [2], namely:

$$\mathrm{rate} \sim \frac{1}{\tau_{\mathrm{c}}} \tag{2}$$

Combining Eqs. (1) and (2) yields an approximate expression for the rate constant of a gelation reaction:

$$k \sim \frac{1}{\tau_{\mathrm{c}} c^{x}} \tag{3}$$

The Arrenhius model describes the temperature dependence of the rate constant of a chemical reaction, $\ln k = \ln A - (E_{\mathrm{a}}/RT)$, where A is the frequency factor [s^{-1}], E_{a} is the energy of activation [J/mol], R is the universal gas constant,

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and T is the absolute temperature. Introducing Eq. (3) into the Arrhenius model yields the expression:

$$\ln\tau_c \sim \ln\frac{1}{Ac^x} + \frac{E_a}{RT} \qquad (4)$$

Thus, a plot of $\ln\tau_c$ versus $1/T$ should yield a downward-sloping line with slope E_a/R and y-intercept $\ln(1/Ac^x)$. This was the case in our experiments, as can be appreciated in Fig. 1. Protein gelation has a negative temperature coefficient, thus, the energy of activation will also be negative.

A family of these Arrhenius plots generated using different initial sol concentrations will intersect at a critical temperature (T_{gel}*), if the E_a is concentration dependent. This peculiar condition was met in our experiments (Fig. 2). We do not have a satisfactory explanation for this unusual behavior—a concentration-dependent energy of activation. However, if the gelation reaction was a combination of several individual reactions with characteristic kinetic behavior, such as aggregation and rearrangement (ageing), it would be theoretically possible to entertain the concept of a concentration dependent energy of activation for the overall reaction. At this particular intersection point, gelation times would be equivalent, and thus $\ln\tau_1 = \ln\tau_2$. Substituting Eq. (4) into the aforementioned condition, and rearrangement, yields an expression for this critical gelation temperature (T^*_{gel}):

$$T^*_{gel} = \frac{\Delta E^{\#}_{12}}{xR\ln\frac{c_2}{c_1}} \qquad (5)$$

where $\Delta E^{\#}_{12}$ corresponds to the difference between the energies of activation for reactions carried out at two different initial sol concentrations. The standard-state Gibbs free energy difference of a reaction is given by $\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} = -RT\ \ln\ K$, where ΔH^{o} is the standard-state enthalpy difference, K is the equilibrium constant, and ΔS^{o} is the standard state entropy difference between products and reactants for a chemical reaction. In the absence of an enthalpic change between products and reactants, this equation reduces to $\Delta S^{o} = R\ln K$, which describes the relationship between the entropy difference between reactants and products and the equilibrium constant for that reaction. The reaction of interest in our treatment is $S_1 \rightleftharpoons S_2$, where S corresponds to the initial sol concentration, and thus $K = [S_2]/[S_1]$. The critical temperature (Eq. (5)) can therefore be expressed as:

$$T^*_{gel} = \frac{\Delta E^{\#}_{12}}{x\Delta S^{o}} \qquad (6)$$

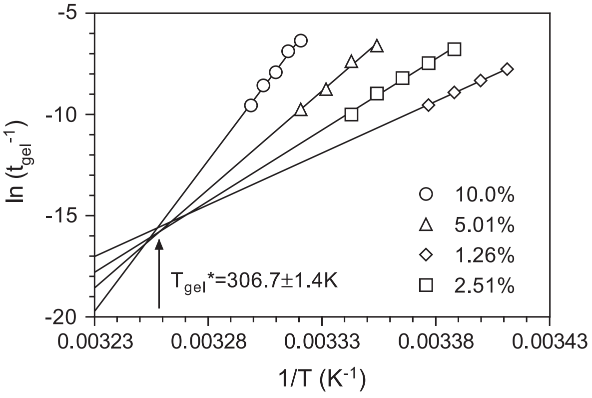

Fig. 1. Arrhenius plot for a gelatin gelation reaction at different temperatures and initial sol concentrations.

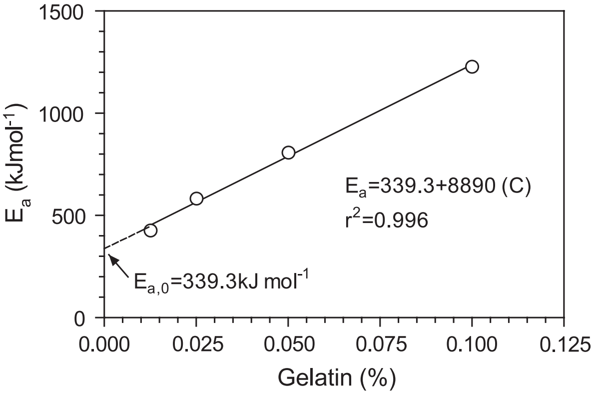

Fig. 2. Variation in the energy of activation for the gelatin gelation reaction as a function of initial sol concentration (C). Notice the linear dependence and the existence of an 'intrinsic' energy of activation, independent of protein concentration.

Thus, this critical gelation temperature equals the ratio of the difference in energies of activation for gelation reactions at different initial sol concentrations to the standard state entropy change related to the change in initial sol concentration.

The relationship between ΔS^{o}_{12} and $\Delta S^{\#}_{12}$ can be derived by considering the thermodynamic cycle depicted in Fig. 3. In this diagram, S represents the initial sol and $S^{\#}$ represents the activated, or transition state, sol undergoing a gelation reaction. The equilibrium constants that describe these reactions are $K_{12} = ([S_2]/[S_1])$, $K^{\#}_{12} = ([S^{\#}_2]/[S^{\#}_1])$, $K^{\#}_1 = ([S^{\#}_1]/[S_1])$, and $K^{\#}_2 = ([S^{\#}_2]/[S_2])$. These equilibrium constants are interrelated, namely $K^{\#}_{12} = (K^{\#}_2/K^{\#}_1)K_{12}$. Since equilibrium constants are not concentration dependent, then $K^{\#}_1/K^{\#}_2 = 1$, and thus $K^{\#}_{12} = K_{12}$. Therefore $\Delta G^{\#}_{12} = \Delta G^{o}_{12}$.

If for this process, the enthalpies of activation for the change in substrate and activated substrate concentrations

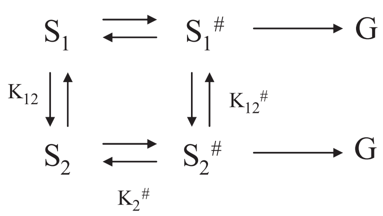

Fig. 3. Thermodynamic cycle depicting the formation of a gel (G) at two different initial polymer sol (S) concentrations.

are the same, i.e., $\Delta H^{\#}_{12} \approx \Delta H_{12}$, then $\Delta S^{\#}_{12} \approx \Delta S^{\circ}_{12}$. Substituting this result into Eq. (6) yields:

$$T^{*}_{\text{gel}} = \frac{\Delta E^{\#}_{12}}{x \Delta S^{\#}_{12}} \tag{7}$$

In order to provide physical meaning to T_{gel}*, we must turn our attention to the Gibbs free energy function in differential form, $\partial G = \partial H - \partial(TS)$. Since $\partial H = \partial E - \partial(PV)$, and $\partial(PV) \approx 0$ for liquids and solids, for isothermal conditions ($\partial T = 0$), the Gibbs equation in differential form can be expressed as $\partial G = \partial E - T\partial S$.

A reaction will be at equilibrium ($\partial G = 0$) at a particular temperature (T_{eq}) where:

$$T_{\text{eq}} = \left(\frac{\partial E}{\partial S} \right)_{P,V,T} \tag{8}$$

Thus, the temperature at which equilibrium will occur equals the ratio of the change in internal energy to the change in entropy for a reaction, at constant pressure, volume and temperature.

Thus, in conclusion, the temperature at which Arrenhius plots for reactions at different initial substrate concentrations intersect equals the temperature at which the sol is at equilibrium with its activated state, as shown in Eqs. (6) and (8). We propose that this temperature corresponds to the maximum gelation temperature.

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