ORIGINAL ARTICLE

A new method to estimate the sol–gel transition entropy in physically gelling systems

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A Clapeyron-type equation is presented to estimate the transition entropy for the sol–gel transition of physical gels, based on simple thermodynamics for the gels under load. The transition entropy and the transition enthalpy were estimated for κ-carrageenan/water and gellan/water systems using this Clapeyron-type equation. For the carrageen systems, the transition entropy per unit gel volume (ΔS_V) remained constant, regardless of the polymer concentration and the species and concentration of the added salts. A similar behavior was also observed for the gellan systems. These results suggest that the structure of the crosslink domains of the gels is almost identical, regardless of the polymer concentration and the species and concentration of the added salts, if the comparison was made with a fixed polysaccharide. The values of ΔS_V obtained in this study were higher than those obtained using calorimetry as reported in the literature; however, the difference was not large.

INTRODUCTION

Polymer gels can be divided into two groups: chemical gels, in which the crosslinks are formed through covalent bonds, and physical gels, in which the crosslinks are formed through non-covalent bonds such as a series of hydrogen bonds and microcrystal domains.[1,2] Solutions of some polymers form physical gels upon cooling if the polymer concentration (c) is higher than a threshold. In this cooling process, the 'freezing point' at which the system loses its fluidity is called the sol–gel transition temperature (T_{tr}) upon cooling. Physical gels melt at a certain temperature upon heating and recover the solution state (or sol state). This melting temperature corresponds to the T_{tr} upon heating. Generally, because these two T_{tr} values are different, a large hysteresis is observed for the sol–gel transition of physical gels.[3,4]

Many studies have clarified the sol–gel transition behavior of physical gels.[1–4] Among the physical gels, much attention has been paid to hydrogels made of polysaccharide in the food industry, and the thermal and rheological properties of various polysaccharide systems have been examined.[2–4] The gelation of polysaccharide/water systems occurs owing to the aggregation of helical domains (single-helix or double-helices) followed by the coil-to-helix transition of the polymer chains.[5–8] In this case, both the transition enthalpy (ΔH) and T_{tr} are related to the dimension and/or structure of the crosslink domains. The aggregation after the helix-to-coil transition is considered to be a type of 'freezing'. Therefore, the sol–gel transition of polysaccharide gels is also owing to the melting/freezing of crosslink domains. The transition temperature T_{tr} can be easily determined using several methods. Dynamic-viscoelasticity measurements upon heating (or cooling) are now widely used for this determination.[7] Available methods for the estimation of ΔH appears to be limited; however,

micro-differential scanning calorimetry (micro-DSC) is often used for the estimation.[8–10] Micro-DSC detects the thermodynamic transition even in a dilute regime where the sol–transition never occurs and instead a sol-sol transition (only a conformational transition such as the helix-coil transition, for example) takes place. Therefore, the ΔH determined using micro-DSC is not purely because of the sol–gel transition but due to the melting/freezing transition of the crosslink domains.

Concerning the sol–gel transition itself, we implicitly know that the entropy (S) may show a discontinuity at the transition point because the translational entropy should disappear by gelation;[1] however, little is known about the real behavior of the derivatives of the free energy.[11] The 'coexistence' of two phases at the transition point is key to understanding the phase equilibrium; however, this coexistance may also cause difficulty in the case of the sol–gel transition because the concept of the coexistence is basically incompatible with the sol–gel transition. Thus, there still remains uncertainty in this type of transition. This uncertainty may imply that the sol–gel transition itself might be regarded as a geometrical transition such as a percolation;[1,12] however, it is still worth searching for a method to provide the transition entropy (or enthalpy) that originates purely from the sol–gel transition. For this purpose, the introduction of mechanical work to the gels is attempted to increase the variance degree of freedom. The aim of this study is twofold: one is to formulate an equation to provide the entropy change at the transition for physical gels under load, as in the case of the volume phase transition of polymer gels,[13,14] and the second is to apply the above equation to κ-carrageenan/water and gellan/water systems to verify the applicability of the proposed method.

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THEORETICAL APPROACH

Here, we focus on the sol–gel transition of physical gels under load. Let $G(T, f)$ be the free energy of the gels defined by a Legendre transform of the internal energy (U) as

$$G(T, \ f) = U(S, \ L) - TS - f \cdot L \tag{1}$$

where T is the temperature, f is the external (uniaxial) force and L is the displacement vector. The work by the pressure is assumed to be negligible and therefore the infinitesimal change of U (dU) is given by d$U = T$d$S + f \cdot$dL. If the gel under load (force f) 'coexists' with the sol at T, then the gel and the sol must satisfy the equilibrium condition:

$$G_{gel}(T, \ f) = G_{sol}(T, \ f) \tag{2}$$

where $G_{gel}(T, f)$ and $G_{sol}(T, f)$ are the $G(T, f)$ of the gel and the sol, respectively. In the sol phase, f vanishes at equilibrium because the sol is a liquid; therefore, $G_{sol}(T, f)$ can be written as $G_{sol}(T, f) = G_{sol}(T)$, which simplifies the equilibrium condition to

$$G_{gel}(T, \ f) = G_{sol}(T) \tag{3}$$

If the coexistence is also assumed at another point ($T + dT$, $f + df$), then the equilibrium condition at this point is given by

$$G_{gel}(T + dT, \ f + df) = G_{sol}(T + dT) \tag{4}$$

An equation determining the slope of the coexistence curve (or phase boundary) is obtained from equations (3) and (4) as

$$\Delta S dT + L_{gel} \cdot df = 0 \tag{5}$$

where $\Delta S = (S_{gel} - S_{sol})$ with $S_{gel} = (\partial G_{gel}/\partial T)_f$, $S_{sol} = dG_{sol}/dT$, and $L_{gel} = (\partial G_{gel}/\partial f)_T$. Assuming that the shape of the gel is cylindrical and f acts downwards on the circular area of the cylinder, we can re-write equation (5) as

$$-\frac{\Delta S}{V_{tr}} dT = \frac{L_{gel}}{h_0 - L_{gel}} \frac{df}{s_{tr}} = \frac{h_0 - h_{tr}}{h_{tr}} \frac{df}{s_{tr}} \tag{6}$$

where L_{gel} and df are defined by $L_{gel} = |L_{gel}|$ and d$f = |$d$f|$, respectively. The quantities h_0 and h_{tr} are the initial height of the gel and the height at the transition temperature, respectively. V_{tr} and s_{tr} are the volume and the force-acting area at the transition temperature, respectively. For h_{tr}, we have $h_{tr} = h_0 - L_{gel}$ and we also have $V_{tr} = h_{tr} s_{tr}$ for V_{tr}. Equation (6) can be re-written as

$$-\Delta S_V = \varepsilon \left(\frac{d\widetilde{\sigma}}{dT}\right)_{coex} \tag{7}$$

where d$\widetilde{\sigma}$ is given by d$\widetilde{\sigma} = df/s_{tr}$ and ε is defined by

$$\varepsilon = \frac{h_0 - h_{tr}}{h_{tr}} \tag{8}$$

The quantity ε is the critical strain for the transition and $\widetilde{\sigma}$ is the true stress. The subscript 'coex' in equation (7) stands for the coexistence curve. The quantity ΔS_V in equation (7) is defined by $\Delta S_V = \Delta S/V_{tr}$ and corresponds to the transition entropy per unit volume. Equation (7) states that the change in entropy at the sol–gel transition point, which we call the transition entropy, is determined by T_{tr}, ε and the slope of the coexistence curve (d$\widetilde{\sigma}/$d$T)_{coex}$; this equation is quite similar to the Clapeyron equation. Because we can expect the relationship $\Delta S_V = \Delta H_V/T_{tr}$, equation (7) can also be converted to the following expression with the transition enthalpy per unit volume (ΔH_V)

$$-\frac{\Delta H_V}{T_{tr}} = \varepsilon \left(\frac{d\widetilde{\sigma}}{dT}\right)_{coex} \tag{9}$$

EXPERIMENTAL PROCEDURE

Powdery κ-carrageenan and gellan were purchased from Tokyo Chemical Industry (Tokyo, Japan), and Wako (Osaka, Japan), respectively, and both were used without further purification. Table 1 summarizes the metal content of the polysaccharides analyzed using ICP-AES (inductively coupled plasma-atomic emission spectroscopy). The polysaccharide hydrogels were prepared by using pure water or salt solutions as solvents. The salts used were NaCl and KCl, which were purchased from Wako. First, the polysaccharide solutions were prepared at 80 °C and poured into a mold to obtain cylindrical samples. Gelation was performed by keeping the solutions at 5 °C for 12–18 h. After removing the gels from the mold, the cylindrical samples were maintained in the solvent at 25 °C for ~ 20 min for equilibration, and then initial diameter (d_0) and initial height (h_0) of the samples were measured. Table 2 summarizes the sample-code, polymer concentration (c), concentration of added salt (c_s), initial diameter (d_0) and initial height (h_0) of the samples. The sample code is composed of two blocks: the left block indicates the type of polysaccharide used (C; carragenan: G; Gellan) and the value of ten times the polymer concentration, and the right block indicates the type of salt used in the solvent (Na; NaCl: K; KCl) and the salt concentration in mM. A blank in the right block indicates that the pure water was used as the solvent.

The cylindrical sample was set in a transparent rectangular container that was filled with the same solvent as used for the sample preparation. A plastic (acrylic glass) plate was mounted on the upper side of the gel, and then metal weights were added on the plate. The compression force (f) acting on the gel was controlled by the metal weights, and a correction by buoyancy was made for the plate and the weights. The transparent container was then settled in a water bath. The temperature of the gel and the surrounding solvent in the container was finely controlled by controlling the water temperature in the bath. The temperature of the gel and the solvent was raised stepwise by 1 °C, and the typical heating rate was approximately 1 °C per 10 min. Preliminary tests were performed to obtain a rough estimate of T_{tr}, and then the experiments proceeded at a temperature lower than the preliminary T_{tr} by ~ 3–4 °C. The transition temperature T_{tr} was defined as $T_{tr} = T_{max} + (1/2)$, where

Table 1 The metal ion content of the polysaccharides analyzed using ICP-AES

	Na^+/ wt%	K^+/ wt%	Ca^{2+}/ wt%	Mg^{2+}/ wt%
κ-carrageenan	2.00	4.8	0.35	—
Gellan	0.46	3.6	0.31	0.089

Table 2 The sample code, polymer concentration (c), concentration of added salt (c_s), initial diameter (d_0) and initial height (h_0) of the samples
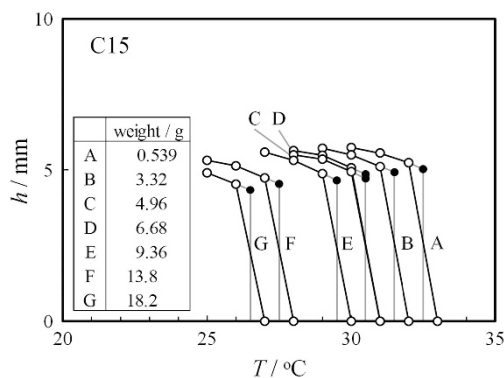
Sample code	c /wt%	c_s/mM	d_0/mm	h_0/mm
C15	1.5	—	10.03	10.08
C20	2.0	—	10.03	10.08
C15-Na25	1.5	25	10.13	10.08
C15-Na50	1.5	50	10.08	10.10
C20-Na25	2.0	25	10.10	10.08
C15-K25	1.5	25	10.03	10.05
C15-K50	1.5	50	10.03	10.03
C20-K25	2.0	25	10.07	10.07
G15	1.5	—	10.30	10.08
G20	2.0	—	10.27	10.10
G10-Na25	1.0	25	10.18	10.10
G10-Na50	1.0	50	10.10	10.07
G15-Na25	1.5	25	10.12	10.08
G10-K25	1.0	25	10.20	10.10
G10-K35	1.0	35	10.37	10.10

T_{max} is the maximum (highest) survival temperature of the gels upon heating at 1 °C intervals. The height of the gel at T, $h(T)$ was monitored during heating using a CCD (charged coupled device) camera with a DVD (digital versatile disc) recorder. Because $\widetilde{\sigma}$ defined in the previous section is the true stress, experimental values of $\widetilde{\sigma}$ were calculated by $\widetilde{\sigma} = f/s_{tr}$ with the assumptions $s_{tr} = s_0 h_0/h_{tr}$. Here, s_0 is the initial force-acting area given by $s_0 = \pi d_0^2/4$, and h_{tr} was estimated by extrapolation using $h(T_{max} - 1)$ and $h(T_{max})$.

RESULTS AND DISCUSSION

Figure 1 shows h plotted against T for the κ-carrageenan hydrogel C15. At a constant f, as traced by a solid line, h monotonically decreases with increasing T and finally reaches the point $h = 0$, where the hydrogel sample melted completely and spread out in the bath. By setting this temperature as $(T_{max} + 1)$, the experimental transition temperature T_{tr} is defined as $T_{tr} = T_{max} + (1/2)$ because the temperature was controlled in an interval of 1 °C. The determined points of T_{tr} for various forces are shown by filled symbols in the figure, indicating that T_{tr} decreases with increasing f. This behavior is also observed for the other κ-carrageenan gel samples. In Figure 2, the h vs T plots of the gellan hydrogel G15 are shown. The value of c for this sample is 1.5 wt%, which is identical to that of the gellan gel shown in Figure 1. As is the case of C15, the T_{tr} of this ample also decreases with increasing f; however, the T_{tr} for gellan is much higher than that for κ-carrageenan (more than 10 °C higher).

Figure 3 shows the $\widetilde{\sigma}$ dependence of T_{tr} for the κ-carrageenan gels. For all the gel samples, the T_{tr} linearly decreases with increasing $\widetilde{\sigma}$, and the slope appears to be almost identical for all the gel samples. As seen from equation (7) and equation (9), this slope corresponds to

$(\partial T/\partial \widetilde{\sigma})_{coex}$. Similar plots for the gellan gels are shown in Figure 4. The vertical axis differs in magnification between panel (a) and panel (b); however, the slope becomes identical for all of the samples. This slope value is slightly higher compared with that for the κ-carrageenan gels, although we do not know the reason at present. It should be recalled that each line in Figures 3 and 4 also becomes a type of phase boundary of the corresponding gel sample. The sol phase is the region above the line, whereas the gel phase is the region below the line. In Figure 5, ε is plotted against $\widetilde{\sigma}$ for C15 and G15 as examples. Because ε expresses the ratio of the compressed length to the retained one (see equation (8)) it is reasonable that ε increases with increasing $\widetilde{\sigma}$ for both gels. The non-zero values of the intercept originate from the deformation of gels owing to their own weight; however, the difference

Figure 3 $\widetilde{\sigma}$ dependence of T_{tr} for the κ-carrageenan gels.
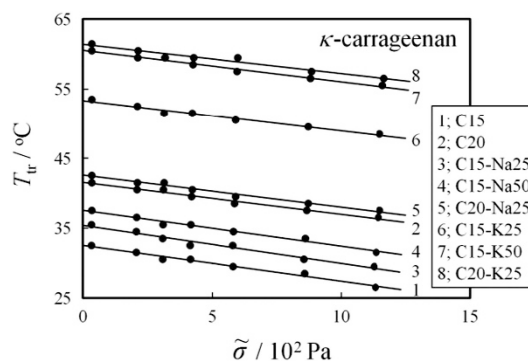

Figure 1 T dependence of h for C15 under load. Symbols A–G differ in applied weight.
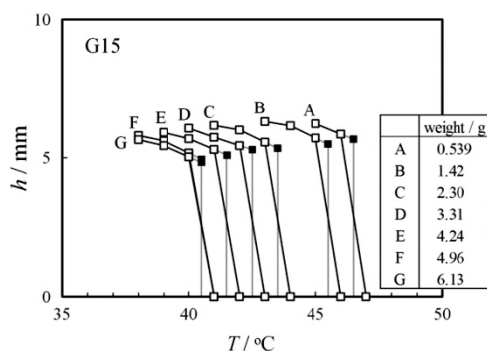
Figure 2 T dependence of h for G15 under load. Symbols A–G differ in applied weight.
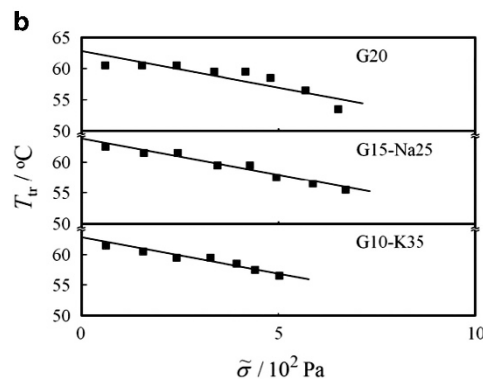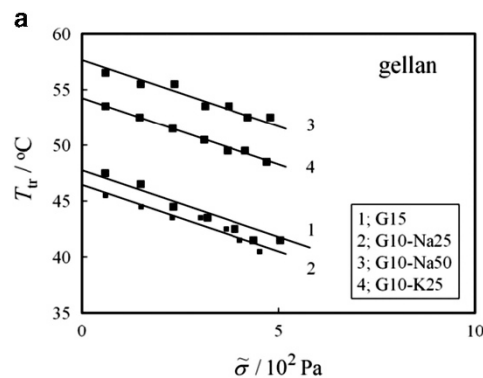
Figure 4 $\widetilde{\sigma}$ dependence of T_{tr} for the gellan gels: (**a**) plots for four samples with lower T_{tr}. The small filled symbol represents G10-K25; (**b**) separate plots for three samples with higher and lower T_{tr}.
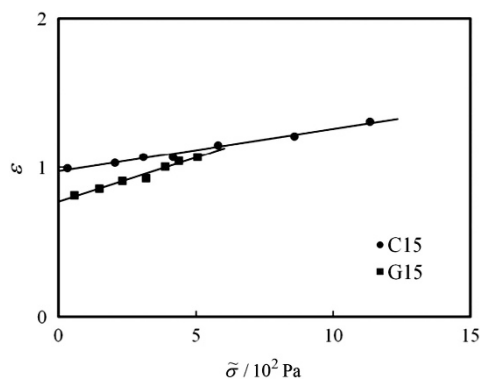
Figure 5 $\tilde{\sigma}$ dependence of ε for C15 and G15.

Figure 7 Normalized transition enthalpy ΔH_V plotted against T_{tr} for the κ-carrageenan gels (circles) and the gellan gels (squares).
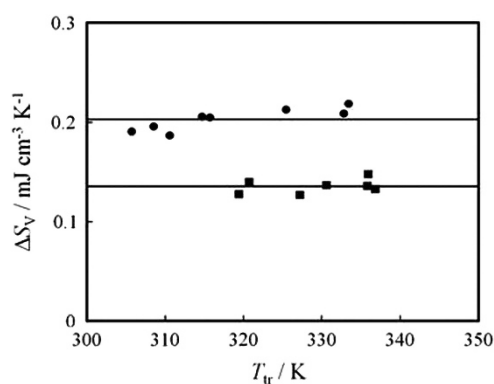

Figure 6 Normalized transition entropy ΔS_V plotted against T_{tr} for the κ-carrageenan gels (circles) and the gellan gels (squares).

Table 3 T_{tr}, ΔS_V and ΔH_V for the κ-carrageenan and gellan gels

Sample	T_{tr}/K	$\Delta S_V/mJ$	$\Delta H_V/mJ\,cm^{-3}$
C15	305.7	0.19	58
C20	314.7	0.21	65
C15-Na25	308.5	0.20	60
C15-Na50	310.6	0.19	58
C20-Na25	315.7	0.21	65
C15-K25	325.4	0.21	69
C15-K50	332.8	0.21	70
C20-K25	333.4	0.22	73
G15	321.4	0.14	45
G20	336.3	0.15	50
G10-Na25	318.5	0.13	41
G10-Na50	331.3	0.14	45
G15-Na25	336.7	0.13	45
G10-K25	327.4	0.13	42
G10-K35	335.4	0.14	46

in these values is not large. The higher slope for gellan reflects the fact that the gellan gel is softer than the carrageenan gel.

Although, ΔS_V defined in this paper depends on force as well as temperature, here we use the limiting values of ΔS_V at $\tilde{\sigma} \to 0$. This limit can be easily made by using ε at $\tilde{\sigma} \to 0$ and the constant value of $(\partial T/\partial \tilde{\sigma})_{coex}$. In Figure 6, ΔS_V at $\tilde{\sigma} \to 0$ is plotted against T_{tr} for the κ-carrageenan gels and the gellan gels. The data points for each of the gels remain constant, independently of T_{tr}. The upper line represents the average values for the carrageenan gels (average $\Delta S_V = 0.20$ mJ-cm^{-3}K^{-1}), and the lower line corresponds to the average of the gellan gels (average $\Delta S_V = 0.14$ mJ cm^{-3} K^{-1}). The difference in the ΔS_V between the two groups mainly originates from the difference in $(\partial T/\partial \tilde{\sigma})_{coex}$. As previously stated, the structure of the crosslink domains is still controversial for polysaccharide gels; however, aggregates of double-helices are widely considered to function as crosslinks.[5,7,8] The fact that ΔS_V remains constant in an individual group suggests that the structure of the aggregates prior to melting is almost identical, regardless of polymer concentration, as well as, the species and concentration of added salts if the polysaccharide species is fixed. However, the different polysaccharide systems provide different ΔS_V values, which indicates that there exists no regularity such as a Richard's rule governing the physical gels. In Figure 7, ΔH_V converted from ΔS_V and T_{tr} is re-plotted against T_{tr}. Here, each line corresponds to the average of ΔS_V in the previous figure. Interestingly, the κ-carrageenan group shows a higher ΔH_V than the gellan group when compared at the same T_{tr}. The numerical values of T_{tr}, ΔS_V and ΔH_V
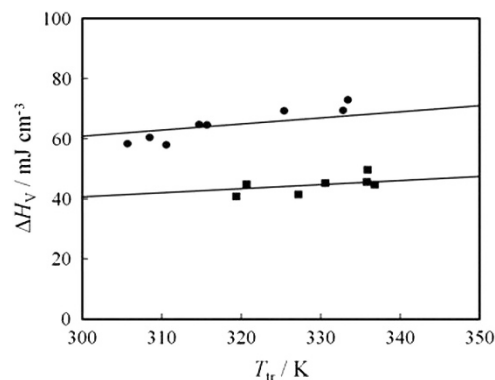
for the polysaccharide gels obtained in this study are summarized in Table 3.

Oakenfull *et al.*[9] have reported the transition temperature and the transition enthalpy for the sol–gel transition of *k*-carrageenan systems. Using their data for a 0.5 wt% system, we can report $\Delta S_V = 0.16$ mJ cm^{-3} K^{-1}. Del Carmen Núñez-Santiago and Tecante have also reported that $\Delta S_V = 0.11$ mJ cm^{-3} K^{-1} if we use the data for a 0.5 wt% system. Both values are lower than the average ΔS_V estimated in this study. Miyoshi and Nishinari[7] have reported similar data for a potassium-type gellan in salt solutions. Converting their values for the 1.0 wt% system into ΔS_V we have 0.076 mJ cm^{-3} K^{-1} for the gellan gel. Thus, the ΔS_V obtained in this study is high compared with those obtained using calorimetry; however, the difference is not large despite the differences in the sample characteristics. This difference might be expected because ΔS_V by micro-DSC reflects only the heat of fusion of the helical domains. This should be clarified by further studies; however, the method presented here is useful for the estimation of the transition entropy (and enthalpy) of physical gels.

CONCLUSIONS

A Clapeyron-type equation for the sol–gel transition of physical gels was formulated, and the transition entropy, as well as, the transition enthalpy was also estimated for κ-carrageenan/water and gellan/water systems based on this equation. For the carrageen gels, the ΔS_V

remained constant regardless of polymer concentration, as well as, the species and concentration of added salts. A similar behavior was observed for the gellan gels. These results suggest that the structure of the crosslink domains of the gels is almost identical, regardless of polymer concentration and the species and concentration of added salts for a fixed polysaccharide. However, because the ΔS_V depended on the type of polysaccharide, there existed no regularity such as a Richard's rule for the polysaccharide gels. The value of ΔS_V obtained in this study was higher than those obtained using calorimetry; however, the difference was not large. We have shown that the Clapeyron-type equation presented here is useful for the estimation of the sol–gel transition entropy (and enthalpy) of physical gels.

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