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A zipper model approach to the thermoreversible gel-sol transition

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Résumé. — La transition gel-sol est assimilée à un processus simple d’ouverture des zones de jonction macromoléculaires semblable à l’ouverture d’une « fermeture éclair ». Cette analogie a déjà été proposée pour expliquer la transition hélice-pelote ou la fusion de l’acide désoxyribonucléique. Le profil expérimental des pics endothermiques qui accompagnent la transition gel-sol lors d’une analyse enthalpique différentielle a pu être ajusté en utilisant ce modèle.

Abstract. — The gel-sol transition of thermo-reversible gels is examined theoretically by using a zipper model which has been used for explaining the helix-coil transition and the melting of deoxyribonucleic acid (DNA). The endothermic peaks in a heating curve of differential scanning calorimetry for various thermoreversible gels are analysed by this treatment.

Introduction.

The dissolution of thermo-reversible gels has been studied over many years not only because of its scientific interest but also because of its practical importance in food processing and in many other industrial applications [1]. Eldridge and Ferry [2] found that the plot of the logarithm of the concentration $\log c$ versus the inverse of the melting temperature $1/T_m$ ($T_m$ in degrees Kelvin), and the plot of logarithm of the molecular weight, $\log M_w$ versus $1/T_m$ were both almost linear for gelatin gels. Using van’t Hoff’s law, they proposed a method to determine the heat absorbed on forming a mole of junction zones.

Tobolsky proposed a theory of dissolution of gels based on the highly swollen network model [3]. It seems, however, difficult to compare his theory with experiments.

Differential scanning calorimetry (DSC) has been used to study the gel-sol transition for thermo-reversible gels. Endothermic peaks arising from the gel-to-sol transition as well as exothermic peaks arising from the sol-to-gel transition have been observed in heating and cooling DSC curves respectively by many investigators [4-11]. The heat absorbed per unit time $dQ/dt$ is given by $C \frac{dT}{dt}$, where $C$ is the heat capacity. In the heating DSC
measurements, $dT/dt$ is positive, then the endothermic peak is equivalent to the maximum of
the heat capacity. In the cooling DSC measurements, $dT/dt$ is negative, then the exothermic
peak is again equivalent to the maximum of $C$.

In the present work, we propose a method of phenomenological analysis of the gel-sol
transition by means of a zipper model which has been previously applied to explain a helix-
coil transition [12-14].

**Zipper model and junction zones.**

It has been widely accepted that most thermo-reversible gels consist of somewhat crystalline
regions, called junction zones, and somewhat amorphous regions. The structure of junction
zones depends on the molecules which form the gels; e.g. junction zones of gelatin gels are
thought to consist of triple helices [15] and those of agarose gels are believed to be a
substantial association of double helices [16]. As a model for these structures, we may assume
such junction zones as the association of molecular zippers standing for a rigid ordered
molecular structure such as helices or extended molecules. A single zipper with $N$ links is
shown in figure 1, where broken lines represent secondary bondings such as hydrogen bonds.

Now, we assume that a junction zone consists of either an association of helices (single,
double or triple) or that of rod-like molecules (Fig. 2a). As in the case of the mixture of
galactomannan (such as locust bean gum) and xanthan solutions, where each component does
not form a gel when they are not mixed, the structure of junction zones is supposed to be the
association of xanthan helical molecules and mannan backbones [17, 18] (Fig. 2b). Both of
these gels can be regarded as gels consisting of zippers of one kind whether molecules which
construct junction zones are the same or not. The molecular forces which make these helices
or rods aggregate are generally believed to be secondary forces such as hydrogen bonds rather
than covalent bonds because the disruption of the covalent bond needs much higher energy
than experimentally observed values. We can, therefore, simulate the dissolution of gels as an
opening process of molecular zippers. We treat a molecular zipper of $N$ parallel links that can
be opened from both ends. When the links $1, 2, ..., p$ are all open, the energy required to
open the $p + 1$ st link is assumed to be $E$. We suppose that each open link can assume
$G$ orientations, i.e., the open state of a link is $G$-fold degenerate, corresponding to the
rotational freedom of a link. These assumptions are the same as those used for the
explanation of the melting of deoxyribonucleic acid (DNA) or helix-coil transition [12-14].
Fig. 2. — (a) Gels consisting of zippers of one kind. Gels consist of microcrystalline regions and amorphous regions. The former is called junction zones, and consist of association of molecules with ordered structure. (b) Gels consisting of zippers of one kind. Schematic representation of a mixed gel of galactomannan whose backbone is shown by a zigzag and xanthan shown by a double helix (proposed by Dea).

The partition function for such a single zipper is given by

\[ \zeta = \sum_{p=0}^{N-1} (p+1) G^p \exp \left( -pE/\tau \right) \] (1)

where \( \tau = kT \). If the chain is long enough, the terminal contribution may be ignored and

\[ \zeta = \frac{[1 - (N+1)x^N + Nx^{N+1}]}{(1-x)^2} \]

\[ x = G \exp \left( -E/\tau \right) \] (2)

is easily obtained from equation (1).

Now, we consider a system consisting of \( N \) single zippers each of which has \( N \) links. The partition function \( Z \) of this system is given by

\[ Z = \zeta^N. \] (3)

Since the heat capacity \( C \) of this system is given by

\[ C = kT^2 \frac{\partial^2}{\partial T^2} \log Z + 2kT \frac{\partial}{\partial T} \log Z \] (4)

the substitution of (2), (3) into (4) leads to

\[ \frac{C}{k} = N \left( \log \frac{G}{x} \right)^2 \left[ \frac{2x}{1-x} + \frac{N(N+1)x^N[-x^{N+1} + (N+1)x - N]}{[1 - (N+1)x^N + Nx^{N+1}]^2} \right]. \] (5)

When the interaction among different components is not strong as in the case of blend gels of agarose and gelatin, the gels formed on cooling may be thought as a phase separated gel as shown in figure 3. We consider here the case in which junction zones consist of associations with \( n \) different kinds of (not molecules but) zippers. Then, \( n \) is not necessarily equal to the
Fig. 3. — Gels consisting of various zippers (phase separated). When two gel-forming macromolecules are mixed, and form a gel, the gel consists of separated two regions if these two macromolecules do not interact so strongly.

number of molecular species. Let $N_1$, $N_2$, ..., $N_n$ be the number of links of single zippers of various kinds 1, 2, ..., $n$ respectively. We assume that a gel consists of $N'_1$ single zippers of the kind 1 and $N'_2$ single zippers of the second kind 2, and so on. The heat capacity of such a system is written as

$$\frac{C}{k} = \sum_i C_i$$

where $C_i$ is given by equation (5).

Some numerical results and discussion.

As stated above, the order of magnitude of bonding energy may be taken as that of a hydrogen bond, i.e. $E_i \approx 2000 \text{ K}$. As for the parameter $G_i$, it will decrease with increasing concentration because the mobility of an opened link will be more constrained at higher concentrations. When the temperature is raised, the volume of the gel increases, and $G$ will also increase because the restriction on the motion of the links will be reduced. However, it is hopeless to derive the functional form of $G(c, T)$ by using microscopic model because of the extremely complicated structures of thermo-reversible gels. Strictly speaking, moreover, the value of $G$ may change in course of successive openings for a single zipper. These points will be discussed later.

The heat capacity $C$ given by equation (5) as a function of temperature is expressed by a horn-shaped curve having a single peak. In order to see its dependence on $G$, $E$, and
N, examples are shown in figures 4a-4c. For the sake of comparison, the curve corresponding to \( G = 1000, E = 2500 \) K and \( N = 100 \) is superimposed in each of these figures. Figure 4a shows the \( G \) dependence of \( C \) with \( E_1 = 2000 \) K, \( E_2 = 2500 \) K, \( N_1 = N_2 = 100 \), \( G_2 = 1 \) 000 and various \( N'_1 \) and \( N'_2 \). \( G_1 \) is changed from 500 to 1 000 (from Fig. 4a(1) to Fig. 4a(4)) and the other parameters are fixed. The higher temperature peak position is mainly determined by \( G_2(<G_1) \) and not shifted by \( G_1 \). The lower temperature peak is determined by \( G_1 \) and is shifted to higher temperatures with decreasing \( G_1 \). Since the value of \( G \) represents the rotational freedom of a link, this is quite reasonable. Figure 4b shows the \( E \) dependence of \( C \) as a function of temperature with \( E_2 = 2500 \) K, \( G_1 = G_2 = 1000 \), \( N_1 = N_2 = 100 \) and various \( N'_1 \) and \( N'_2 \). \( E_1 \) is changed from 2 200 K to 2 460 K and the other parameters are fixed. The higher temperature peak position is mainly determined by \( E_2 (>E_1) \) and not shifted by \( E_1 \). As is expected, the lower temperature peak shifts to higher temperatures with increasing \( E_1 \). Figure 4c shows the \( N \) dependence of \( C \) as a function of temperature with \( E_1 = 2000 \) K, \( E_2 = 2500 \) K, \( N_2 = 100 \), \( G_1 = G_2 = 1000 \), and various \( N'_1 \) and \( N'_2 \). \( N_1 \) is changed from 50 to 400. The peak temperature is mainly determined by \( E_i \) and \( G_i \) and is shifted only slightly by \( N_i \). The lower temperature peak shifts to higher temperatures with increasing \( N_1 \) which is expected from empirical formulae of Eldridge-Ferry (2) : higher the molecular weight, the higher the melting point of gels.

These numerical results can explain experimental results accumulated for many years (19). When the concentration of gels increases, the mobility of chain molecules decreases, and then the degeneracy \( G \) will decrease as mentioned above. As a result, the peak of the heat capacity shifts to higher temperatures. This is in accordance with Eldridge-Ferry's empirical formulae.

It is well known that the melting temperature \( T_m \) of a thermo-reversible gel in its heating DSC curve appears at a higher temperature than the setting temperature \( T_s \) in its cooling DSC curve. When the temperature is raised, \( G \) would start from the lower value \( G_g \) corresponding to the gel state. Then, the gel will expand, which will give rise to an increase in the rotational freedom. On the contrary, when the temperature is lowered from higher temperatures than the melting point, \( G \) will start from the higher value \( G_s \) corresponding to the sol state. Therefore, the opening of molecular zippers begins to occur at small \( G \) values in heating process, while gelation by cooling will take place with decreasing \( G \) which starts from large \( G \) values at higher temperatures. Then, the average effective value of \( G \) is small in heating and is large in cooling. As a first approximation, therefore, we can say that the melting peak temperature \( T_m \) is determined by certain average \( \bar{G}_g \) of \( G \) for gel state and the setting temperature \( T_s \) is determined by an average \( \bar{G}_s \) of \( G \) for sol state. Apparently, \( \bar{G}_g < \bar{G}_s \), hence, \( T_m \) is expected to be higher than \( T_s \).

In the case of heating, the transition caused by the opening of the zippers will start as soon as the temperature arrives at the tail of the \( C - T \) curve corresponding to \( G = G_g \). In cooling, on the contrary, the pair-wise coupling cannot start so easily because of the difficulty for a long molecule to find its partner in appropriate positions for the zipper construction. Hence a state like supercooling may take place in the course of cooling. It is, therefore, reasonable that the transition is sharper in cooling than in heating as has been observed for agarose gels [10].

Comparison with experiments.

1. KAPPA-CARRAGEENAN GELS. — The solid curve in figure 5 shows an experimental heating DSC curve for 0.6 % kappa-carrageenan gel [20]. Since the endothermic peak is very sharp, we can fit the calculated curve to the experimental one by choosing \( E = 2290 \) K,
Fig. 4.
Fig. 4. — (a) $G$ dependence of the heat capacity as a function of the temperature calculated by equation (6) with $n = 2$. Only $G_1$ is changed. $E_1 = 2000$ K, $E_2 = 2500$ K, $N_1 = N_2 = 100, G_2 = 1000$ are fixed for all the cases. a: $N'_1 = 450, N'_2 = 50$ ; b: $N'_1 = 300, N'_2 = 200$ ; c: $N'_1 = 150, N'_2 = 350$. (b) $E$ dependence of the heat capacity as a function of the temperature calculated by equation (8) with $n = 2$. Only $E_1$ is changed. $E_2 = 2500$ K, $G_1 = G_2 = 1000, N_1 = N_2 = 100$ are fixed for all the cases. a: $N'_1 = 450, N'_2 = 50$ ; b: $N'_1 = 300, N'_2 = 200$ ; c: $N'_1 = 150, N'_2 = 350$. (c) $N$ dependence of the heat capacity as a function of the temperature calculated by equation (6) with $n = 2$. Only $N_1$ is changed. $E_1 = 2000$ K, $E_2 = 2500$ K, $N_2 = 100, G_1 = G_2 = 200$ are fixed for all the cases. a: $N'_1 = 450, N'_2 = 50$ ; b: $N'_1 = 300, N'_2 = 200$ ; c: $N'_1 = 150, N'_2 = 350$. (2) a, b, c the same as in figure 4c(1). (3) a: $N'_1 = 1800, N'_2 = 200$ ; b: $N'_1 = 1200, N'_2 = 800$ ; c: $N'_1 = 600, N'_2 = 1400$, (4) a: $N'_1 = 3600, N'_2 = 400$ ; b: $N'_1 = 2400, N'_2 = 1600$ ; c: $N'_1 = 1200, N'_2 = 2800$.

$N = 1850, N = 100$, and $G = 1000$ in equation (5). The calculated result is shown by the dotted curve in figure 5.

2. POLY (VINYL ALCOHOL) GELS. — The experimentally obtained heating DSC curves for poly(vinyl alcohol) (PVA) gels, prepared by repeating freeze-thaw cycles [7], are shown in figure 6 by solid curves. The lower curve is for PVA with the degree of polymerisation (DP) = 1000, and the upper curve is for PVA with DP = 2400, respectively. Choosing $n = 2$ and substituting values of parameters $E_1 = E_2 = 2300$ K, $N_1 = N_2 = 100, G_1 = 820, G_2 = 1100$, $N'_1 = 3900, N'_2 = 1200$ into equation (6), we obtain the lower dot-and-dash curve in figure 6 which is slimmer than the observed curve shown by the lower solid curve in the same figure.
The solid curve represents the observed heating DSC curve of a 0.6% kappa-carrageenan gel. The dotted curve is obtained by using equation (5) with $E = 2290 \text{ K}$, $N_1 = 1850$, $N = 100$, $G = 1000$.

Fig. 6. — Solid curves represent the observed heating DSC curves of poly(vinyl alcohol) gels (the upper curve: DP = 2400, the lower curve: DP = 1000). A lower dot and line curve is obtained by using equation (6) with $n = 2$ choosing parameters, $E_1 = E_2 = 2300 \text{ K}$, $N_1 = N_2 = 100$, $G_1 = 820$, $G_2 = 1100$, $N_1' = 3900$, $N_2' = 1200$. An upper dot and line curve is obtained by using equation (6) with $n = 2$ choosing $E_1 = 2265 \text{ K}$, $E_2 = 2365 \text{ K}$, $N_1' = 1750$, $N_2' = 3250$, $N_1 = N_2 = 240$, $G_1 = 980$, $G_2 = 950$. A dotted curve for a lower curve is obtained by using equation (6) with $n = 8$ and substituting $E_1 = \cdots = E_8 = 2300 \text{ K}$, $G_1 = 820$, $G_2 = 900$, $G_3 = 960$, $G_4 = 1030$, $G_5 = 1100$, $G_6 = 1200$, $G_7 = 1300$, $G_8 = 1400$, $N_1' = 3600$, $N_2' = 600$, $N_3' = 450$, $N_4' = 500$, $N_5' = 750$, $N_6' = 350$, $N_7' = 150$, $N_8' = 100$, $N_1 = \cdots = N_8 = 100$, into equation (6).

As is seen in figure 4c, the endothermic peak caused by the gel-to-sol transition shifts to higher temperatures with increasing degree of polymerisation. The number of links $N_i$ must increase and the rotational freedom of the constituting links may decrease with increasing degree of polymerisation. Based on such consideration, another fitting has been tried by choosing $E_1 = 2265 \text{ K}$, $E_2 = 2365 \text{ K}$, $N_1 = N_2 = 1750$, $N_2' = 3250$, $N_1 = N_2 = 240$, $G_1 = 980$, $G_2 = 950$. The result is given by the upper dot-and-dash curve, which is again slimmer than the experimental curve shown by the upper solid curve in figure 6.

As stated earlier, the $G$ value may not be fixed even for a single zipper and it might have certain distribution around a mean value even at a fixed temperature. In order to take these situations into account, $n$ has to be further increased anyhow in the fitting, though it is certain that the parameters, as well as their numbers, cannot be determined uniquely. As an example, the result of calculation is shown in figure 6 as the dotted curve which is obtained by choosing $n = 8$ and substituting $E_1 = \cdots = E_8 = 2300 \text{ K}$, $G_1 = 820$, $G_2 = 900$, $G_3 = 960$, $G_4 = 1030$, $G_5 = 1100$, $G_6 = 1200$, $G_7 = 1300$, $G_8 = 1400$, $N_1' = 3600$, $N_2' = 600$, $N_3' = 450$, $N_4' = 500$, $N_5' = 750$, $N_6' = 350$, $N_7' = 150$, $N_8' = 100$, $N_1 = \cdots = N_8 = 100$, into equation (6), for a PVA gel (DP = 1000). The fitting is fairly good.

Similar results can be obtained also by taking into account various different energy values $E_i$. In fact, it is sometimes more appropriate to assume that some zippers may be opened at
lower energies and others should be released at higher energies. Such situations are often observed in polymeric crystals, i.e., two different crystallites of poly (γ-benzyl-l-glutamate) in benzyl alcohol were observed by light microscopy, and they disappear at two different temperatures [21].

3. KONJAC GLUCOMANNAN-KAPPA-CARRAGEENAN GELS. — The solid curve in figure 7 shows a heating DSC curve for a 0.42 % kappa-carrageenan-0.18 % konjac glucomannan blend gel (20). The endotherm is very broad. It may be attributed to the formation of zippers with different energies for link-opening or to a distribution of the degeneracy $G$. Choosing $n = 8$ again and substituting $E_1 = E_2 = \cdots = E_8 = 2000$ K, $G_1 = 370$, $G_2 = 390$, $G_3 = 410$, $G_4 = 440$, $G_5 = 470$, $G_6 = 490$, $G_7 = 520$, $G_8 = 550$, $N_1 = 1000$, $N_2 = 250$, $N_3 = 150$, $N_4 = 250$, $N_5 = 150$, $N_6 = 50$, $N_7 = 75$, $N_8 = 50$, $N_1 = \cdots = N_8 = 100$, into equation (6), we can get fairly good agreement of the calculated curve with the observed one.

Experimental.

The DSC curve for kappa-carrageenan gels in figure 5 and that for konjac glucomannan-kappa-carrageenan gels in figure 7 were obtained by a Setaram micro DSC « batch and flow » calorimeter. Approximately 1 ml of the sample was accurately weighed into the DSC pan and the reference pan filled with exactly the same amount of distilled water. The two pans were then placed inside the calorimeter, heated to 85 °C to ensure the sample was in the form of a homogeneous solution and cooled to the starting temperature. Then, the temperature was raised at 1 °C/min. The details of the experimental procedure will be described elsewhere [20].

The DSC curves for PVA gels in figure 6 were obtained by a sensitive DSC SSC 560U from Seiko Instruments & Electronics Ltd. 41.5 ± 0.1 mg of PVA gel sample was sealed into a 70 μl silver pan. Distilled water was used as a reference material. The temperature was raised at 2 °C/min from 5 °C. The details of the experimental procedure were described in the reference [7].

Conclusion.

It is shown that the observed DSC endothermic peaks of the thermoreversible gels are well simulated by simple calculations based on the zipper model, if the rotational freedom of links, the bonding energy, and the number of links in thermo-reversible gels are chosen appropriately. Experimental data suggest that bonding energy in many thermo-reversible gels is of the order of the hydrogen bonds, i.e. about 2000 K. Assuming this value for bonding
energy, we can estimate the rotational freedom of links and the number of links by curve fitting. Therefore, we can obtain a clue to the structure of junction zones in thermoreversible gels. Needless to say, the number of fitting parameters should be as small as possible. Otherwise one cannot determine their values uniquely.

In some cases, however, the observed peaks are too broad to simulate by an assembly of a few kinds of zippers. This may be attributed to the variety of the parameter values, which might be expressed by continuous distributions. In this respect, it is shown that such a distribution can be well replaced by a finite number of species of zippers. Since the choice of parameter values is by no means unique, they should not be taken too literally. In order to testify these results, therefore, much more informations are urgently awaited as for the structure of junction zones.

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