On the Origin of the Formation and Stability of Physical Gels of Di-*O*-benzylidene-D-sorbitol

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Received: October 8, 1998; In Final Form: January 8, 1999

The thermal and fluorescence properties of gels formed from 1,3:2,4-di-*O*-benzylidene-D-sorbitol (DBS) and 1,3:2,4:5,6-tri-*O*-benzylidene-D-sorbitol (TBS) in ethylene glycol (EG) and other alcoholic solvents were investigated. The fluorescence of the benzylidene ground state dimer was observed even in the solution state, indicating that DBS and TBS tend to aggregate in EG. The concentration dependence of the DBS−EG and TBS−EG fluorescence spectra shows that the main structures of DBS and TBS fibers are identical with one another and that each ten-member bicyclo ring overlaps with other rings: the 1,3-*O*-benzylidene and 2,4-*O*-benzylidene groups overlap with each of the other units. The fluorescence results show that some 5,6-*O*-benzylidene groups of TBS interacted with 1,3- and 2,4-benzylidene groups, which is the reason that TBS−EG gels are less stable than DBS−EG gels. The very slow heating of DBS−EG gels showed that needlelike crystals formed at around 370 K for DBS concentrations of 1, 5, and 10%. This indicates that the hydrogen bonding of EG with DBS fibers is cut off at around 370 K. The solvent dependence of enthalpies for melting, ΔH_m, and setting, ΔH_s, of DBS gels was measured. Since (i) enthalpies were not dependent on each intrinsic property of the solvent and (ii) plots of both ΔH_s versus the density of hydroxy groups of the solvent and ΔH_m versus the density of all the groups that can form hydrogen bonds were found to give straight lines, DBS fibers are concluded to mainly consist of DBS molecules and to be supported by solvent molecules on their surfaces.

I. Introduction

Thermoreversible physical gelation has been the subject of many studies.[1,2] In particular, there is growing interest in gelation induced by the addition of small molecules to organic solvents. The reported gelator molecules include molecules having a wide structural diversity: 12-hydroxystearic acid,[3,4] semifluorinated *n*-alkanes,[5] steroids,[6,7] aromatic-linked steroids (ALS),[8−10] compounds with long alkyl chains,[11−15] lecithin,[16] calixarenes,[17] cyclodextrin,[18] depsipeptides,[19] and dipeptides.[20−22] However, the main reason for the induction of gelation has not been identified. For example, a long-chain alkylamide of *N*-benzyloxycarbonyl-L-valyl-L-valine can cause physical gelation.[23] However, it is not obvious whether the main cause of gel formation is the long alkyl chain or the steric structure of the dipeptides.

1,3:2,4-Di-*O*-benzylidene-D-sorbitol (DBS)[24] is a derivative of the natural sugar alcohol D-glucitol and is known as a chiral oil gelator since Yamamoto discovered the gelation of DBS in alcoholic solvents in 1942.[25] Recently, Yamasaki et al. reported the gel properties of DBS, using several measurements such as circular dichroism, microscopy, ^{13}C solid state NMR, and so on.[26−30] According to Yamasaki et al., the DBS−ethylene glycol (EG) gel state is metastable, having two kinds of mesophases: one is a crystalline phase consisting of the spherulitic texture, and the other is an isotropic mesophase comprising a network-like structure between the spherulites.[26]

To clarify the main reason for the stability of DBS gels, we studied in detail the thermal and rheological properties of gels formed from EG solutions of DBS and its derivatives, 2,4-(mono)-*O*-benzylidene-D-sorbitol (MBS), and 1,3:2,4:5,6-tri-*O*-benzylidene-D-sorbitol (TBS).[31,32] The results clearly showed that the ease with which gels formed from sorbitol derivatives in EG, and the stability of these gels, were in the order DBS−EG > TBS−EG > MBS−EG. Because the number of hydroxy groups is 4 for MBS, 2 for DBS, and 0 for TBS, it was concluded that the number of hydroxy groups in a sorbitol derivative is not an important factor in the formation and stability of gels made with these derivatives. The hydrophobic interaction among benzylidene groups is also not a crucial factor. Accordingly, it is concluded that the main factor in the formation of stable gels is the chemical structure of the six-member ring of MBS, or the ten-member bicyclo ring of DBS, that facilitates the formation of crystals. The importance of the molecular weight architecture is suggested in the formation of stable physical gels of other low molecular weight compounds.[7]

The application of fluorescence spectroscopy is growing remarkably as a powerful and effective tool to study the physical and chemical behavior of aggregated states, such as gels or solids.[33−36] Since fluorescence techniques are not only highly sensitive but also nondestructive, they are useful for monitoring changes in the microenvironment. We have already succeeded in applying the fluorescence probe method to some thermoreversible gel systems.[37−39] In the present study we applied fluorescence spectroscopy to obtain information on the microenvironment of DBS and TBS gels. It is expected that the results will be useful to clarify the cause of the formation and stabilization of the DBS gel system.

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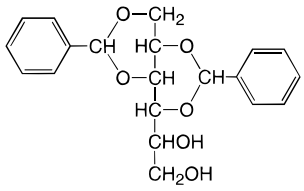
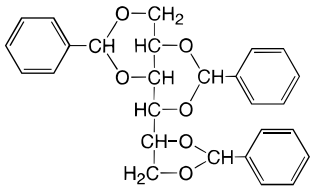
10.1021/jp984018w CCC: $18.00
Published on Web 03/13/1999



1,3: 2,4-di-*O*-benzylidene-D-sorbitol (DBS)



1,3: 2,4: 5,6-tri-*O*-benzylidene-D-sorbitol (TBS)

Figure 1. Chemical structures of DBS and TBS.

II. Experimental Section

Materials. Figure 1 shows the chemical structure of 1,3:2,4-di-*O*-benzylidene-D-sorbitol (DBS) and 1,3:2,4:5,6-tri-*O*-benzylidene-D-sorbitol (TBS). DBS and TBS were prepared as previously reported.[31] Ethylene glycol (EG), diethylene glycol (DG), triethylene glycol (TRG), tetraethylene glycol (TEG), and glycerol (GL) (Wako Co., all special grade) were used as solvents without further purification.

Fluorescence Measurements. Fluorescence spectra and fluorescence excitation spectra were measured on a Hitachi F-4500 spectrofluorometer. Fluorescence measurements for the gels were carried out in a quartz cell with an optical path length of 1 mm for their aerated solutions. A gel was prepared in a cell by heating DBS or TBS and solvent to 140−160 °C and then placing them in a −23 °C freezer overnight. A cell was set at 45° to the exciting beam. The excitation wavelength was set at 259 nm. The sample temperature was controlled by an Oxford DN1704 cryostat with an ITC-4 digital temperature controller, which can regulate to better than ±0.1 K. Independent temperature measurement was carried out by means of a second thermocouple and a potentiometer. All samples were kept at each set temperature, and spectra were run repeatedly for 2−10 h even after perfect duplication was obtained, since one of the main aims of the present work was to determine the time required for equilibrium.

Differential Scanning Calorimetry (DSC) Measurements. DSC measurements of gels were done with a Sensitive DSC SSC 5200 (Seiko Instruments & Electronics, Ltd.). A sample (45 ± 0.1 mg) of each of the gels was sealed into silver pans of 70 μL: samples were weighed to within 0.01 mg using an M_1-20 analytical balance (Chou Keiryouki Co.). Each disposable silver pan without a sample was dried thoroughly at 300 °C for 30 min before the measurements. We must emphasize that this treatment is quite important, because steep exothermic peaks due to silver appear at about 150 °C without the preheating treatment. Distilled water was used as a reference material and the weight was made equal (within ±0.1 mg) to that of the sample gel to obtain a flat baseline. To choose the scanning conditions, the DSC curves of a DBS−EG gel were measured at heating and cooling rates of 0.5, 1, 2, and 4 °C/min. There were no large differences in the peak temperatures obtained with the 0.5, 1, and 2 °C/min scanning rates. The DSC curves obtained by using a rate of 0.5 °C/min were so broad that it was not easy to identify a peak temperature. Thus, the following conditions were chosen. For heating, the temperature was raised from 5 °C at a rate of 2 °C/min to observe an endothermic peak accompanying the transition. For cooling, the temperature of the sample was raised to a temperature higher than the peak temperature of gel melting, T_m, by 10−15 °C, was kept there for 15 min, and then was lowered at a rate of 2 °C/min.

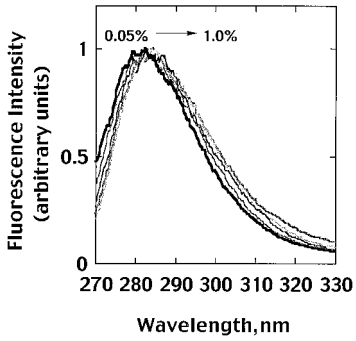


Figure 2. Fluorescence spectra of DBS−EG at several concentrations; 0.05 (black bold line), 0.1, 0.3, 0.5, and 1% (gray bold line). All the spectra are normalized to the peak. The excitation wavelength is 259 nm.

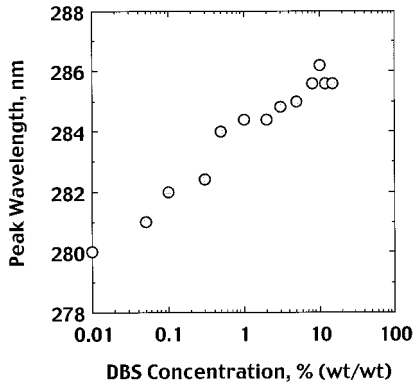


Figure 3. Dependence of DBS concentration on fluorescence peak wavelength of DBS−EG. The band-pass of the emission light was 1 nm. Gelation takes place between 0.3 and 0.5%.

III. Results and Discussion

Fluorescence Behavior of DBS−EG Gels. Figure 2 shows the fluorescence spectra of DBS−EG at lower concentrations. With an increase in DBS concentration, the whole spectrum for each of the concentrations was found to shift to the red. Thus, the fluorescence of DBS is considered to be a measure of aggregation. Figure 3 demonstrates the concentration dependence of the fluorescence peak wavelength and the point of inflection is observed between 0.3 and 0.5%. In fact, the spectrum at 0.5% is different from that at 0.3%, while it is nearly the same as that at 1.0%. DBS−EG was found to form gels at room temperature at a concentration above 0.5%,[40] which was previously reported by Yamasaki et al.[27] Thus, as it turns out, the fluorescence behavior of DBS−EG is concluded to correspond to not only a microscopic change such as formation of finite-sized aggregates but also a more macroscopic change such as gelation.

Figure 4 shows the UV absorption spectra of DBS−EG at various concentrations. With an increase in DBS concentration, the spectra became broad together with the disappearance of some fine structure, and a new broad absorption appeared in the longer wavelength region. The change in absorption and fluorescence can be explained by the formation of a ground

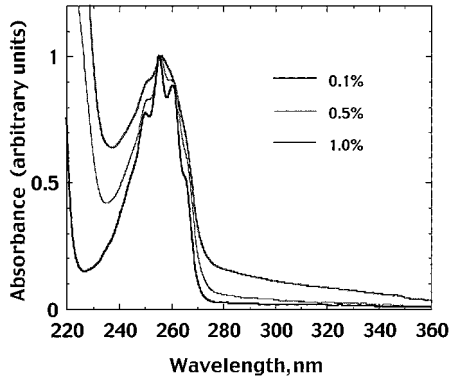


Figure 4. Ultraviolet absorption spectra of DBS−EG at concentrations of 0.1, 0.5, and 1%. The spectra were measured using a quartz cell with an optical path length of 1 mm. All the spectra are normalized to the peak around 260 nm.

state dimer between the two benzylidene moieties at higher concentrations. The formation of a ground state dimer is due to the resonance of a π-electron between the two aromatic groups, thus two benzylidene groups are assumed to be in a parallel configuration within a distance of at most 0.35 nm. A ground state dimer has been reported for quite a few systems having aromatic groups, for example, poly(ethylene terephthalate)[41−43] and gels of benzylcellulose.[38,44] The same behavior was also observed in a DBS−GL gel system.

The photophysical results shown in Figures 2−4 indicate that (i) the distance between the benzylidene groups of two DBS molecules probably is less than 0.35 nm in the fibers made up with DBS molecules, (ii) DBS molecules can readily aggregate in alcoholic solutions such as EG and GL, and (iii) DBS forms a sort of aggregate even at concentrations lower than 0.05%.

It is not easy to assume the size of aggregates, although our fluorescence technique is quite sensitive to short range interactions. Note that ground state dimers of benzylidene groups are not readily formed when two benzylidene groups can move such as in fluid solution, because the van der Waals force between two benzylidene groups is not strong enough to keep them fixed.[36] What we can comment here is that the aggregates formed in EG or GL solutions of DBS have regular orientation to fix several benzylidene groups as to form ground state dimers, and that their stability happened to strongly depend on the gelation.

Next we measured the temperature dependence of DBS−EG fluorescence spectra from room temperature to 430 K. The temperature of a gel was controlled in a cryostat and was raised in 5 K steps after making sure that an equilibrium state was attained at each temperature. Figure 5 shows the fluorescence spectra of 5% DBS−EG at various temperatures. The time required to reach a consistent spectrum at each temperature, including the time required to change temperatures, was usually less than 30 min. The decrease in fluorescence intensity with heating is quite natural since the radiationless deactivation process is accelerated by heat. All the spectra, when normalized to the peak, were almost identical with one another except in the longer wavelength region. The most important change observed in Figure 5 is the sudden rise of the baseline from 370 K, which was due to the appearance of needlelike crystals. The DSC measurements of DBS−EG gels at a rate of 1 or 2 °C/min did not show any evidence of recrystallization.[31] Thus, the recrystallization is probably due to a very slow heating process, which was achieved through the use of a cryostat. The slow heating is assumed to promote the dissociation of solvent

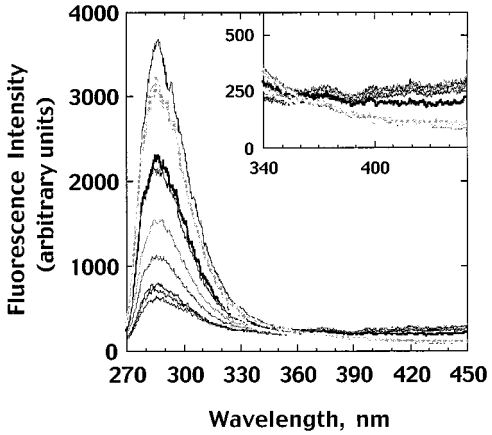


Figure 5. Temperature dependence of fluorescence spectra for 5% DBS−EG: the spectra are 350, 360, 365, 370 (black bold line), 375, 380, 385, 390, 395, and 400 K in the order of decreasing peak intensity. The baseline at longer wavelengths rises at temperatures higher than 370 K.

molecules from DBS fibers at 370 K, which is the temperature at which hydrogen bonding of EG with DBS fibers is cut off.

To test this assumption, we measured the concentration dependence of T_{rc}, the temperature at which a crystal appears and the base of the spectrum begins to rise. The T_{rc}'s were determined to be 370 K for 1, 5, and 10% DBS−EG, while recrystallization was not observable for 0.01% DBS−EG, which did not form a gel. The fact that the T_{rc} for different concentrations of DBS were identical would suggest that the interaction energy of DBS fibers with EG is mainly due to hydrogen bonding and is constant.

The band-pass of the emission light could not be made narrow enough for the temperature change measurement (actually, 2.5 nm), since DBS fluorescence intensities at higher temperatures were so weak that a smaller band-pass would result in excessive noise. Thus, the information on wavelength is not always reliable. However, the peak wavelengths of 5% and 10% DBS−EG at 410 K were still 284 and 285 nm, respectively.[45] This suggests that DBS molecules are in an aggregated form in fluid solution even at 400 K.

Two conclusions can be drawn from the results shown in Figure 5: (i) the cutoff temperature for hydrogen bonding of EG with DBS fibers is 370 K, and (ii) DBS molecules are still aggregated in EG at temperatures above T_{rc} and below the melting temperature of DBS crystals (210−212 °C).[46]

Fluorescence Behavior of TBS−EG Gels. We have already shown that TBS−EG gels are not as stable as DBS−EG gels on the basis of the viscoelastic and DSC measurements.[31] Figure 6 shows the fluorescence spectra of TBS−EG at several concentrations. Up to a concentration of 1%, the spectrum of TBS−EG, like that of DBS−EG, was shifted to the red. However, above 1% the peak wavelength started to shift to the blue and the fluorescence intensity near 280 nm began to increase. The concentration dependence of peak wavelength is shown in Figure 7.

The red-shift of the peak observed for lower TBS concentrations (Figure 6A) is thought to be identical to that of DBS−EG fluorescence, meaning that the benzylidene groups of two TBS molecules are so close as to form a ground state dimer in the aggregated state or crystal state. DBS fibers are considered to be formed by the overlapping of each benzylidene group with a benzylidene group of another DBS within a distance of 0.35 nm, because emission from the ground state dimer is observed. It is also possible to be described that they are formed by the

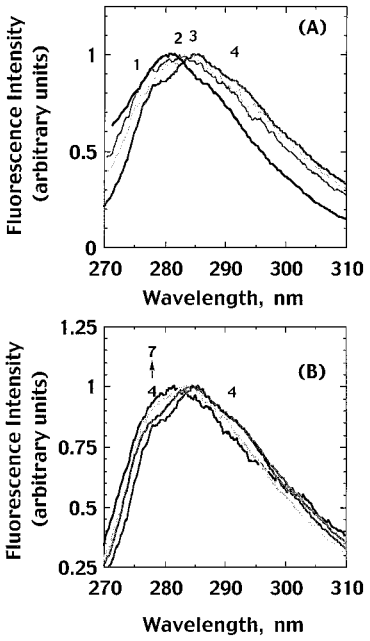


Figure 6. Fluorescence spectra of TBS−EG at several concentrations. (A) lower concentrations of TBS and (B) relatively higher ones of TBS: (1) (black bold line), 0.01%; (2) 0.05%; (3) 0.1%; (4) 0.5% (gray bold line); (5) 1%; (6) 2%; (7) 3% (black bold line). All the spectra are normalized to the peak. The excitation wavelength is 259 nm.

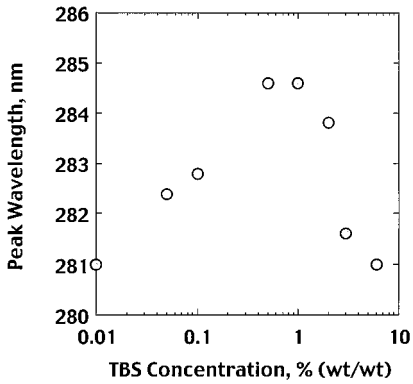


Figure 7. Dependence of TBS concentration on fluorescence peak wavelength of TBS−EG. The band-pass of the emission light was 1 nm.

overlapping of each ten-member bicyclo ring of DBS with the ten-member bicyclo ring of another of DBS. Since the chemical structure of TBS is similar to that of DBS (Figure 1), the stable form of TBS fibers is probably formed by the overlapping of the ten-member bicyclo rings. In this case one benzylidene group, i.e., 5,6-*O*-benzylidene, of TBS would be isolated in an oriented fiber form while two benzylidene groups directly attached to the bicyclo ring take part in the formation of a ground state dimer, as occurs with the two benzylidene groups of DBS. The blue shift and increase in emission near 280 nm at higher TBS concentrations is probably due to the increase in concentration of isolated benzylidene groups, accompanied by an increase in the amount of oriented forms of TBS, such as crystals or fibers. In fact, the intensity of fluorescence at longer wavelengths decreased only slightly.

Figure 8 compares the fluorescence spectra of DBS−EG and TBS−EG at three different concentrations. The discussion above suggests that the formation of TBS fibers is demonstrated by the higher intensity of fluorescence at wavelengths below 280 nm. Figure 8A shows that the two spectra agreed well at 0.5% except for some parts of the spectrum at longer wavelengths of

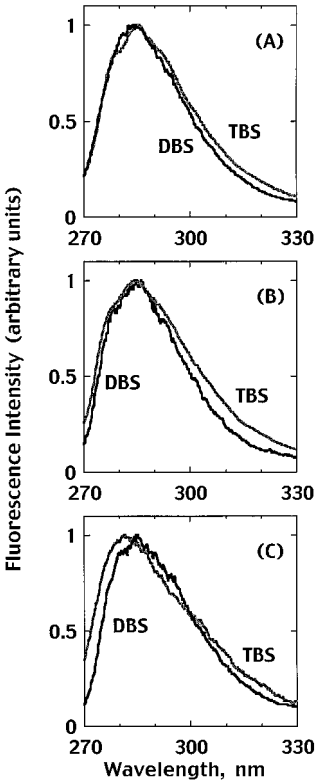


Figure 8. Comparison of fluorescence spectra of DBS−EG and TBS−EG at the same concentration: (A) 0.5%; (B) 1%; (C) 3%. Black line: DBS−EG. Gray line: TBS−EG. All the spectra are normalized to the peak. The excitation wavelength is 259 nm.

TBS−EG, meaning that a greater fraction of TBS is in the form of the ground state dimer but that the fraction in the crystal form is still low. At 1%, where both DBS−EG and TBS−EG form gel, the TBS fluorescence has components at both shorter and longer wavelengths, meaning that TBS fibers are formed at this concentration. In Figure 8C, the formation of fibers having the TBS crystal form can be seen more clearly.

The preceding results explain why TBS fluorescence spectra shifted to the red at lower concentrations and to the blue at higher ones. The spectra in Figure 8A also help to explain why TBS−EG gels are a little weak and unstable compared to DBS−EG gels: the higher intensity of TBS−EG at longer wavelengths shows the formation of the ground state dimer between the 5,6-*O*-benzylidene group and the benzylidene group at the other position. The existence of this component must distort TBS fibers. In other words, the third benzylidene group of a TBS molecule prevents the formation of regular TBS fibers by interacting with other benzylidene groups of another TBS molecule.

In a previous paper,[31] we suggested that the main reason for the stabilization of sorbitol gels in alcoholic solvents is not simply due to hydrogen bonding or hydrophobic interactions among benzylidene groups but rather to a delicate balance of chemical structure that facilitates the formation of crystals. The fluorescence results obtained with the TBS−EG gels offer strong evidence of this. The symmetric structure of a DBS molecule, which has a rigid and chiral ten-member ring symmetrically connected with two benzylidene groups in equatorial positions, is considered to be the most important reason that DBS forms more stable gels than does TBS.

Solvent Effect on Thermal Properties of DBS−EG Gels. We have shown by using fluorescence measurements that (A) the main factor in the formation of stable gels in this study is the

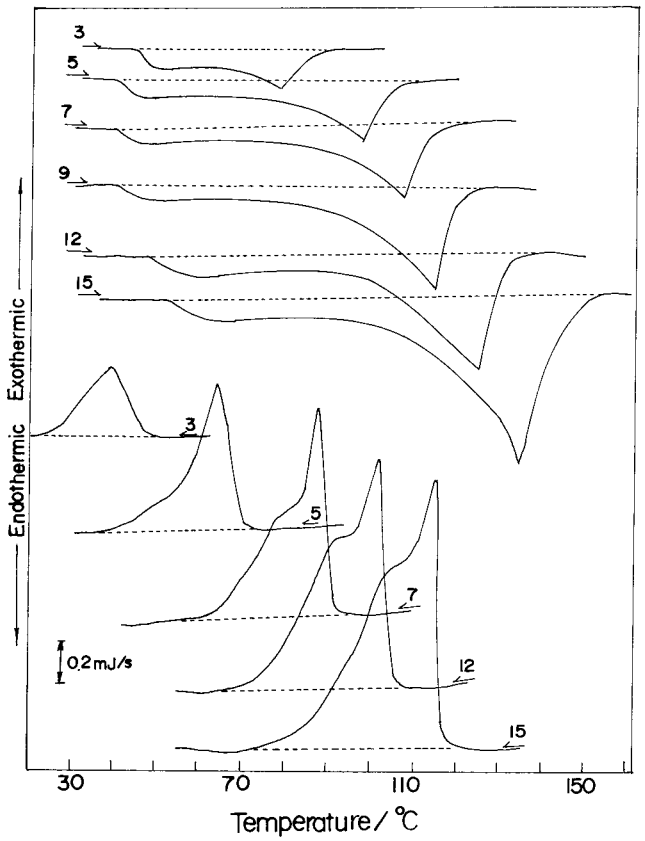


Figure 9. Heating and cooling DSC curves of DBS−TRG gels of various concentrations. The figures beside the curves represent the concentration in percentage (wt/wt). The broken lines are baselines used for the calculation of enthalpies.

chemical structure of the ten-member bicyclo ring of DBS that facilitates the formation of crystals and (B) the cutoff temperature for hydrogen bonding of EG with DBS fibers is 370 K. The next problem is the relationship between DBS fibers and the solvents. Two models are possible to assume: (I) DBS fibers include a constant portion of solvent inside them, or (II) DBS fibers mainly consist of DBS and solvents only interact with the surface of DBS fibers. The above summary (B) suggests that (II) is more probable. To examine this model, we measured the solvent dependence of the stability of DBS gels.

Figure 9 shows the heating and cooling DSC curves of DBS−TRG gels at different concentrations. In the heating process, an endothermic peak was observed as expected from the gel melting. The peak temperature and the peak area gave the melting temperature of the gel, T_m, and the enthalpy of gel melting, ΔH_m, respectively. With an increase in concentration of DBS (c_{DBS}), T_m became higher and ΔH_m increased. In the cooling process, there was a sharper exothermic peak at the transition from sol to gel. The peak temperature and the peak area gave the setting temperature of the gel, T_s, and the enthalpy of gel forming, ΔH_s, respectively. We tried heating and cooling rates of 0.5, 1, 2, and 4 °C/min and measured the DSC curves of a DBS−EG gel. Although T_s slightly decreased and T_m slightly increased with an increase in a rate between 0.5 and 2 °C/min, the difference was a few degrees at most. The values of ΔH_m and ΔH_s were almost constant at rates between 0.5 and 4 °C/min. Thus, we decided to compare the DSC data obtained for heating and cooling rates of 2 °C/min. With increasing c_{DBS}, both T_s and ΔH_s increased. Table 1 summarizes the values of T_m, T_s, ΔH_m, and ΔH_s obtained from the DSC measurements

TABLE 1. Thermal Properties of DBS−Alcoholic Solvent Gels at Various Concentrations: Temperature of Gel Melting, T_m, Temperature of Gel Setting, T_s, Enthalpies Obtained from the Peak Area of the DSC Curves for Gel Melting, ΔH_m, and for Gel Formation, ΔH_s

concentration (% (w/w))	T_m (K)	T_s (K)	ΔH_m (kJ/mol)	ΔH_s (kJ/mol)
		DBS−EG		
2	359.4	336.0	44.8	44.6
3	369.0	345.9	51.3	46.1
5	381.0	359.0	48.7	44.1
7	386.8	366.0	46.5	43.2
10	396.0	376.4	46.6	43.1
12.5	401.1	383.0	46.1	42.6
15	406.0	389.1	50.6	45.2
20	419.5		58.7	
25	428.3	400.0	61.7	49.4
av			50.5	44.8
		DBS−DG		
3	356.5	321.1	40.6	38.6
5	373.2	343.0	41.5	37.4
7	383.0	356.6	39.4	35.5
9	388.6	364.7	39.0	35.1
12	400.0	376.2	40.3	36.3
15	405.0	383.0	48.2	34.8
20	417.5	393.0	49.8	33.8
av			42.7	35.9
		DBS−TRG		
3	351.4	312.0	37.0	31.4
5	371.2	337.3	33.7	31.0
7	380.6	364.0	36.3	36.3
9	387.9		37.0	34.7
12	397.9	374.6	34.6	31.1
15	407.3	388.3	34.9	31.3
av			35.6	32.6
		DBS−TEG		
3	343.6	303.0	25.1	23.7
5	367.7	331.2	29.4	26.5
7	376.6	343.8	29.2	26.3
9	387.4	357.8	30.2	27.7
12	394.2	371.2	29.5	25.6
av			28.7	26.0
		DBS−GL		
0.5	384.2	349.4	57.3	43.0
1	397.2	362.5	60.8	46.5
2	412.0	382.2	64.4	48.3
3	421.5	392.6	64.4	44.1
4	429.1	402.3	64.4	46.5
5	435.8	408.6	68.7	49.4
av			63.3	46.3

for DBS−EG, DBS−DG, DBS−TRG, DBS−TEG, and DBS−GL gels.

If the above results are dependent on common properties such as the density of hydroxy groups rather than on the intrinsic properties of the solvent, DBS fibers are supported by solvent molecules on their surface, and DBS fibers mainly consist of DBS molecules. Here we define the density of hydroxy groups, [OH], as the molar concentration of hydroxy groups per 1 L:

$$[\mathrm{OH}] = 1000dn/M \qquad (1)$$

where M and d are the molecular weight and density of the solvent, and n is the number of hydroxy groups in the chemical formula of a solvent.

Figure 10 shows the relationships of [OH] with ΔH_m and ΔH_s, both of which were linear: the coefficients of determination are 0.941 for ΔH_m and 0.954 for ΔH_s. Both lines shown in Figure 10 are extrapolated to give almost the same values of

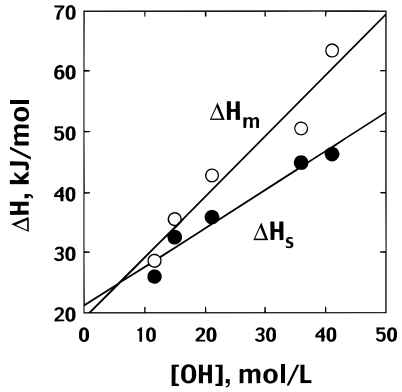


Figure 10. Relationship of density of hydroxy group, [OH], with ΔH_m or ΔH_s. The best fit lines are $\Delta H = 1.01[\mathrm{OH}] + 19.1$ for ΔH_m and $\Delta H = 0.641[\mathrm{OH}] + 21.2$ for ΔH_s.

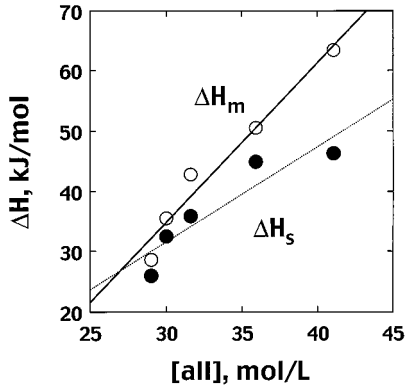


Figure 11. Relationship of density of all the groups that can form hydrogen bonds, [all], with ΔH_m or ΔH_s. The best fit lines are $\Delta H = 2.65[\mathrm{all}] - 44.6$ for ΔH_m and $\Delta H = 1.58[\mathrm{all}] - 15.7$ for ΔH_s.

ΔH at [OH] = 0. The strong dependence on density of hydroxy groups demonstrates that (i) DBS fibers are not formed from a regular DBS−solvent complex, but that (ii) they mainly consist of DBS molecules in the alcoholic solvents used here. In other words, the DBS fibers are assumed to be formed by the DBS microcrystals whose surfaces are surrounded by solvents by way of hydrogen bonding.

We have already reported that the dynamic modulus E' of DBS−EG gels began to increase beyond a certain temperature, meaning that the interaction between the DBS fibers and the EG solvents is strong enough to expand the fibers in the sol area.[31] This behavior supports the existence of the interaction of the alcoholic solvents with the surface of the DBS fibers.

The diameter of the DBS fibers is considered to be short. Yamasaki et al.[29] and Thierry et al.[47] reported it to be 3.2 and 10 nm, respectively, by the electron micrograph measurements. Since the model of a DBS molecule demonstrates[29,31,47] that the distance between two farthest hydrogen atoms in different benzylidene groups is about 1.4 nm, the cross-section of the DBS fibers is assumed to contain a few or at most 10 molecules. Accordingly, the interaction of the solvents with the surface of the DBS fibers is considered to be important. Thus, we deduce that the alcoholic solvents interact with the surface of DBS fibers that mainly consists of DBS molecules.

We would like to comment on the difference of ΔH_m and ΔH_s in the present case. Table 1 shows that most ΔH_m's were larger than ΔH_s's and that the difference increased with an increase in concentration, although some showed the same values of ΔH_m and ΔH_s. This behavior is not always common in thermoreversible gels: for example, Guenet et al. reported that ΔH_m and ΔH_s of agarose gels were virtually the same.[48] We assume that (I) the value of ΔH_s is the net energy based on the gel structure, (II) the difference enthalpy, $(\Delta H_m - \Delta H_s)$, is not neglected when there exists the additional interaction of a network fiber with solvents at low temperatures, and (III) this difference should be small in the case of the gel system where solvents form a regular complex with a network fiber such as a polymer−solvent compound.

In the present work, DBS molecules do not form a molecular compound with solvent molecules. Thus, the DBS fibers and the alcoholic solvents are not always oriented regularly. At low temperatures, the gel state includes various interactions among many different groups. For example, even an oxygen atom with low electron density can participate in hydrogen bonding at low temperatures where the molecular motion of functional groups is so restricted that a functional group can form hydrogen bonding with another group situated nearby. Once hydrogen bonds are formed, they will be kept at a high temperature. Thus, as mentioned previously,[31,38] it is quite natural that the heat required for the gel melting, ΔH_m, should be larger than that released by the stabilization due to gel formation, ΔH_s.

To confirm this experimentally, we attempted to determine the relationship between ΔH_m or ΔH_s and the density of groups that have the ability to form hydrogen bonds. The ether group was included as one of these groups since the oxygen atom of the ether bond can form a hydrogen bond. As in eq 1, we define the density of all the interactive groups, [all], as the molar concentration per 1 L.

$$[\mathrm{all}] = 1000dm/M \qquad (2)$$

where m is the total number of hydroxy and ether groups in the chemical formula of a solvent (2 in EG, 3 in DG, 4 in TRG, 5 in TEG, and 3 in GL).

Figure 11 shows the relationships of [all] with ΔH_m and ΔH_s, both of which were fitted to straight lines: the coefficients of determination are 0.964 for ΔH_m and 0.851 for ΔH_s. We have to admit that the definition of [all] is quite rough because the ability of all the functional groups to form hydrogen bonds is assumed to be the same. However, the relationship of ΔH_m with [all] was found to be better fitted to a straight line than that with [OH], while ΔH_s versus [all] did not give a linear relationship. These results show that our comment on the difference between ΔH_m and ΔH_s is quite reasonable. We would like to emphasize that the case is limited to the system where a network fiber does not regularly form a molecular compound with solvents and where a network fiber has interactive groups with solvent molecules by way of intermolecular interaction such as hydrogen bonding.

IV. Conclusion

The fluorescence measurements showed that the ground state dimer was formed in alcoholic solutions of DBS and TBS. Because the formation of ground state dimers increased with an increase in DBS concentration, the benzylidene groups in DBS fibers or DBS junctions were found to be oriented within a distance of 0.35 nm. Taking into account the symmetric structure of the DBS molecule, DBS fibers are considered to be formed by piling the ten-member bicyclo rings on top of one another: the 1,3-*O*-benzylidene group of one molecule is overlapped with that of another one, while the 2,4-*O*-benzylidene groups of one molecule is overlapped with that of another one. The fluorescence results indicated that DBS molecules are ready

to aggregate in alcoholic solutions such as EG and GL and form a sort of aggregate even at concentrations lower than 0.05%.

The solvent dependence of ΔH_m and ΔH_s of DBS gels indicated that they are not dependent on each intrinsic property of the solvent but rather on the density of groups that are capable of forming hydrogen bonds; in fact a plot of ΔH_s versus [OH] (the density of hydroxy groups of the solvent) and a plot of ΔH_m versus [all] (the density of all groups that can form hydrogen bonds) were found to give straight lines. Moreover, the recrystallization of DBS was observed at 370 K when DBS−EG was heated very slowly by means of a cryostat in order to ensure that an equilibrium state is attained. The temperature did not vary with DBS concentrations between 1 and 10%. These two facts suggest that DBS fibers mainly consist of DBS molecules and are supported by solvent molecules interacting on their surface. A temperature of 370 K is considered to be the cutoff temperature for hydrogen bonding of EG with DBS fibers.

The concentration dependence of the TBS−EG fluorescence spectra shows that the main structure of TBS fibers is identical to that of DBS fibers. In both TBS and DBS, the ten-member bicyclo rings, which are directly joined to two benzylidene groups, overlap with one another. Thus, this structure is the most crucial for forming network fibers, which is supported by solvent molecules. At higher concentrations of TBS−EG, the fluorescence intensity of isolated 5,6-*O*-benzylidene groups greatly increased. However, the fluorescence data clearly showed that some 5,6-*O*-benzylidene groups of TBS interacted with 1,3- and 2,4-benzylidene groups especially at lower concentrations. The overlapping of 5,6-*O*-benzylidene with 1,3- and 2,4-benzylidene groups would distort regularly oriented TBS fibers and would make TBS−EG gels more unstable compared with DBS−EG gels.

In summary, DBS or TBS molecules self-aggregate in alcoholic solutions to form microcrystals or fibers. However, these aggregates can also interact with solvents, since their surfaces have some groups that can form hydrogen bonds. Thus, DBS or TBS fibers, both of which mainly consist of DBS or TBS molecules, are supported by solvent molecules and form gel networks. In the case of DBS, the interaction of EG with the surface of DBS fibers is cut off at nearly 370 K and DBS crystals appear. However, below this temperature, the interaction between the solvent and the DBS fibers does not allow recrystallization but induces the formation of a network.

Thus, the main reason that DBS and TBS in alcoholic solvents form gels is that their symmetrical ten-member bicyclo ring, which two benzylidene groups are directly joined to, can easily form regularly oriented aggregated forms. However, the bicyclo ring is a little too large to crystallize and also has some interactive groups that readily form a hydrogen bond with solvent molecules. We have previously studied thermoreversible gels formed from biopolymers such as polysaccharides[49−53] and cellulose derivatives.[38,44] However, the structure of the junction points and/or the gelation mechanism are still unclear in many systems of biopolymeric physical gels.[54] For this reason, it is important to study the formation of thermoreversible gels by small molecules such as sugar alcohol DBS to clarify the essential features of physical gelation. Presently, we are investigating the gelation behavior of DBS derivatives. It is expected that these studies will provide further evidence that the molecular architecture of these molecules is important.

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