Luminescence Spectra of fluorescein dye in ionic gel near phase transition

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Luminescence spectra of fluorescein dye in ionic gel near phase transition*

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Abstract

We wish to propose a new method for studying the phase transition ($V/V_0 \sim 500$) of an ionic gel by means of the fluorescence observation. It is found that the volume change of the gel with dye is drastic-response to the half-width ($\Delta\nu_{1/2} \sim 950$ Å), peak wavelength ($\Delta\nu_0 \sim 585$ nm) and spectral profile of the fluorescence line. It is also suggested that the big change of spectral width and peak shift may be explained tentatively by assuming a random-electric field to act on the dye molecules in the gel system.

Introduction

A gel is one of the polymers, and is different from other polymers in that it has a cross-linked network.

A gel is an intermediate state of a solid and a liquid. It consists of a polymer network immersed in a fluid. The essential conditions for a gel are the presence of a polymer and the existence of a cross-link between chain polymers to create the cross-linked network. Polymers made up of one or two dimensional structures infinitely swell and disperse, or dissolve, in a solvent, but gel is not dissolved even in a good solvent because of the cross-linked network. This prevents the gel from dispersing in a solvent. Gel plays an important role in various aspects of our everyday life. The familiar gels, for example, are probably jelly, gelatin, rubbers, soft contact lenses, agar, and *tofu*.

It is well known that an ionized gel immersed in a solvent absorbs the solvent and swells greatly.

But recently, Tanaka (1) observed that the collapse, or swelling of the ionized gel under certain conditions was a discrete phenomenon. Tanaka observed the collapse of acrylamide gels upon changing the fluid composition and the temperature and explained the phenomenon in

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terms of mean-field theory based on the extension of Flory's formula for the free energy of gels. Since his observation many studies, both theoretical and experimental (2-15), have been done in this field. The main results obtained by Tanaka and his school in recently years are as follows (1-13).

1) The volume change of gel is a discrete and reversible phenomenon (1,2,3).
2) The phase transition can be explained in terms of the osmotic pressure of the gel (1,3,6).
3) The phase transition is affected by solvent composition, temperature (1,4), electric field (5), and pH (4).

The purpose of this paper is to study the phase transition of gels by means of a fluorescence observation. So, we have been studying the fluorescence spectra of organic dyes in acrylamide gel near phase transition (15). In this paper we wish to report the volume change of acrylamide gel with dye, and the fluorescence spectra of the fluorescein dye in it under desiccation, from its swollen state to the collapse state at room temperature. It is found that the volume change of gel under desiccation is continuous and for shrink factors of 500-fold and 250-fold, the half width and the peak shift increase as the gel shrinks. But after the gel reaches the equilibrium state both the half width and the peak shift suddenly increase, and a new fluorescence band appears, which may be observed in the wavelength range 400 - 500 nm.

Gel Preparation

The gel used in this experiment is acrylamide gel which is very popular for column chromatography in biochemistry and chemistry. Acrylamide gel consists of linear polymer chains of acrylamide molecules cross-linked by bis-acrylamide molecules, which consist of two acrylamide molecules connected together. The interstitial space of the polymer network is filled with water molecules.

The samples were prepared by a similar method to that of Tanaka et al. (3,4,13). Acrylamide ($CH_2CHCONH_2$) (5.0 g), the linear constituent N, N'-methylene-bis-acrylamide ($(CH_2CHCONH_2)_2CH_2$) (0.133 g), the tetra-functional cross-linking constituent N, N, N, N,-tetramethylenediamine ($((CH_3)_2NCH_2)_2$) (TEMED) (240 μl), the accelerator were dissolved at room temperature in distilled and nitrogen-saturated water to a final volume of 100 ml. 1 ml of ammonium persulfate solution $(NH_4)_2S_2O_8$ (40 mg/ml), the initiator, was then added to 25 ml of the former solution. While stirring the solution, several capillary tubes were added. Gelation started in a few minutes and was practically complete within an hour.

The gel was left in the tubes for several hours, and then removed. Separation of the gel from tube wall was affected with a syringe and needle by forcing water between the gel and the wall. The gels formed were immersed in distilled and nitrogen-saturated water for 24 hours in order to wash away any residual acrylamide, bis-acrylamide, ammonium persulfate and TEMED. The gels were then cut into small pieces and immersed in a basic solution of NaOH (0.1 mol) to hydrolyze a portion of the acrylamide groups, $-CONH_2$, into carboxyl groups, -COOH. A quarter of the carboxyl groups are then ionized into carboxyl ions, COO^-, and hydrogen ions, H^+. The polymer network becomes negatively charged, having positive hydrogen

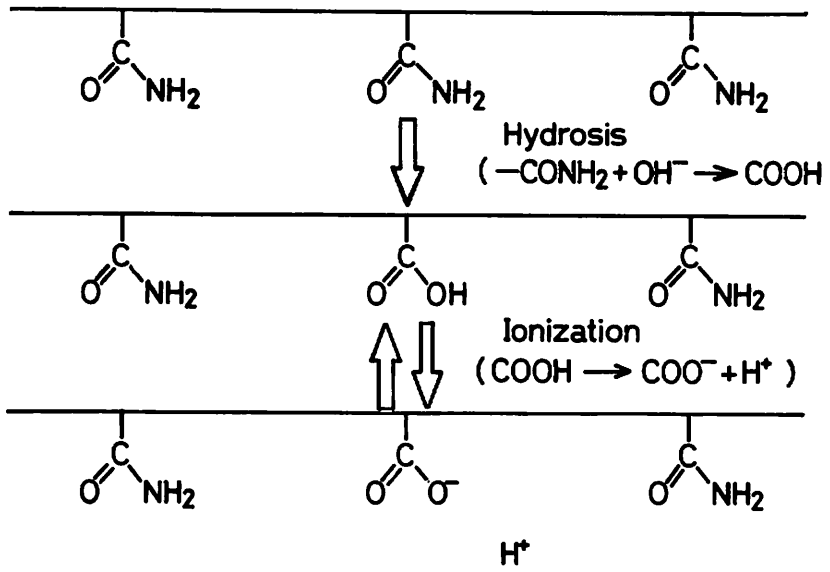

Fig. 1 Hydrozation of acrylamide gel. The acrylamide groups, $-CONH_2$, are hydrolyzed by a basic solution of NaOH into carboxyl groups, -COOH, ($-CONH_2 + OH^- \rightarrow COOH$). The carboxyl groups then are hydrolyzed into carboxyl ions, $-COO^-$, and hydrogen ions, H^+, in the interstitial space ($-COOH \rightarrow -COO^- + H^+$).

ions, H^+, in the interstitial space. The longer the immersion time, the more charged the polymer network becomes. After the hydrolysis the gels were washed in distilled and nitrogen- saturated water for several days. At this stage of sample preparation the gel is greatly swollen. A fully hydrolyzed gel, for example, swells 250 times from the original volume.

The final stage of sample preparation is the impregnation of dye into the gels. To impregnate the dye into the gels, the gels are immersed in a dye solution for several days. Then the dye molecules have diffused completely into the polymer network in the gel. The dye used in this system is fluorescent in dye ($C_{20}H_{12}O_5$) which is dissolved in water with 0.1 mol NaOH. The original dye solution of 5×10^{-3} mol concentration was diluted with water, and then the diluted solution was used to diffuse the dye into the polymer network.

Experimental Results and Discussion

The optical system for fluorescence measurement is shown in Figure 2. The excitation of the sample was accomplished by a high pressure mercury-arc lamp. The volume change was measured by using a simple travelling microscope. The fluorescence spectra and the volume change of the sample were continuously measured under desiccation of the sample at room temperature.

In Figure 3, we plot the degree of swelling as a function of acetone concentration in acetone-water mixture solution for a gel hydrolyzed for 11 days. The volume ratio V/V_0 is the ratio of the final volume, V, to the initial volume, V_0 and is obtained by measuring the initial

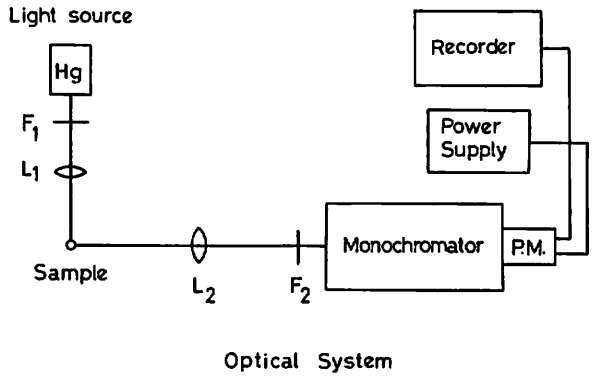

Fig. 2 Optical-system diagram for fluorescence measurement.

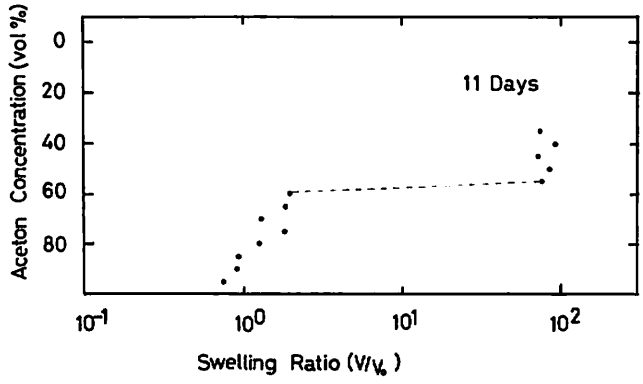

Fig. 3 Swelling curve as a function of acetone concentration for a gel hydrolyzed for 11 days. The critical acetone concentration is 53% and the volume changes a transition of about 80 times.

(d_o) and the final (d) diameter of the gel; i.e., $V/V_o=(d/d_o)^3$. A volume ratio $V/V_o>1$ means that the gel swells, and $V/V_o<1$ means that the gel shrinks. As the aceton concentration is increased the gel gradually shrinks. But, at 53% acetone concentration, the gel suddenly collapses, and remains collapsed at higher acetone concentrations. The degree of volume change at the transition is approximately 80 times.

For a sample hydrolyzed for 11 days and then immersed in 5×10^{-5} mol fluorescein dye solution, the change of volume ratio under desiccation is shown in Figure 4. The rate of volume collapse increases with time, and the volume become constant at about 400 min. The factor of the volume collapse is about 250-fold. In Figure 5, the fluorescein spectra of this sample at different times are shown. The time denotes the period of desiccation and the arrow depicts the time when the gel stopped collapsing. Both half-width and peak-shift increase clearly with time, as the sample shrinks. The spectra early in the desiccation are similar to those of the fluorescein in solvent (0.1 mol NaOH solution). After the gel has stopped collapsing, another new fluorescence band appears in the wavelength range 400 - 500 nm. But in the case of swelling and with

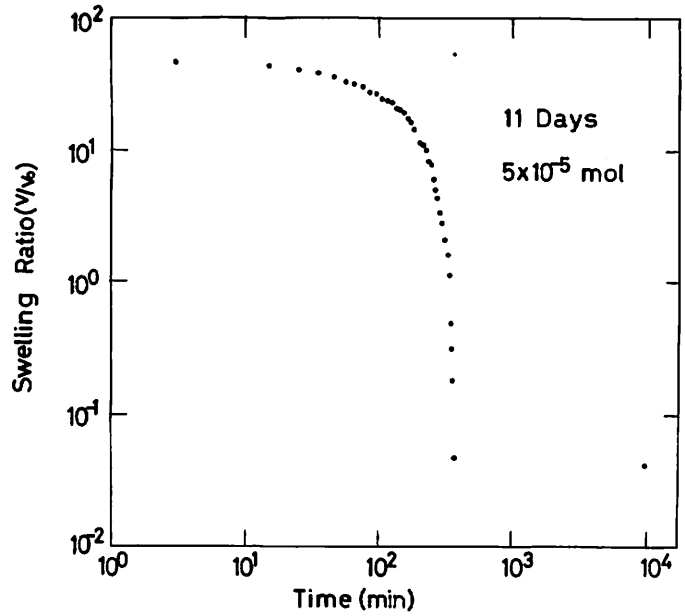

Fig. 4 Swelling ratio curve for a gel hydrolyzed for 11 days and immersed in a dye solution of 5 X 10^{-5} mol concentration. The rate of volume collapse increases with time and the factor of collapse is approximately 500-fold. Equilibrium is reached at about 400 min.

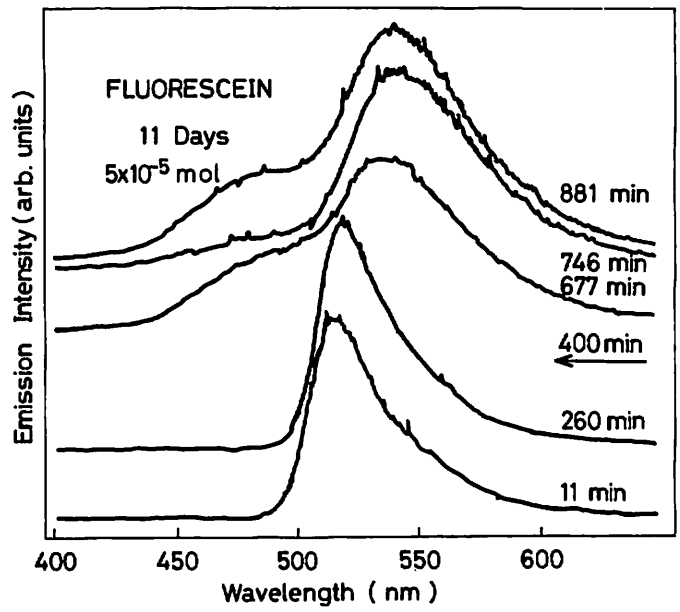

Fig. 5 Temporal change of fluorescence spectra. It is clearly observed the changing of half width and peak wavelength, and also the appearance of new fluorescence band in the wavelength range of 400 - 500 nm.

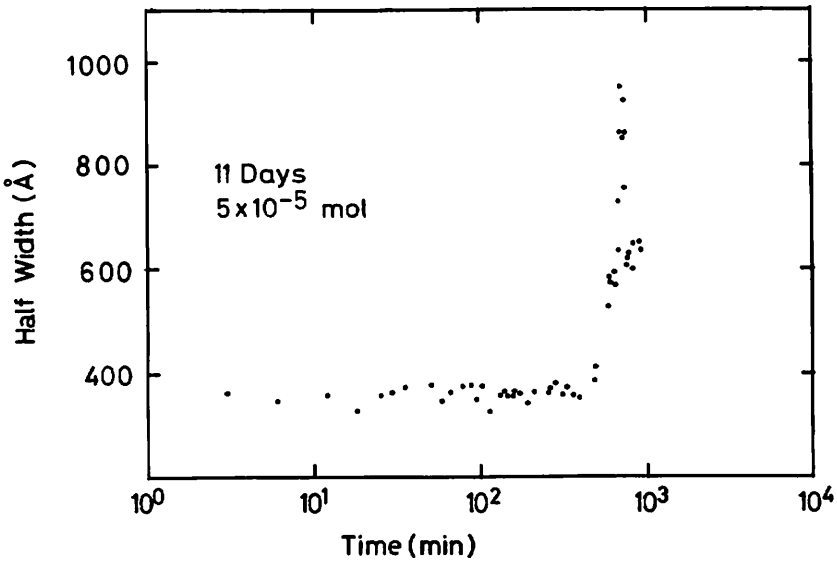

Fig. 6 Half width versus the period of desiccation. The half width increases slowly as the gel shrinks until the gel reaches equilibrium. After the equilibrium it begins to increase suddenly. Some large values (range from 650 Å to 950 Å) are caused by the appearance of the new band.

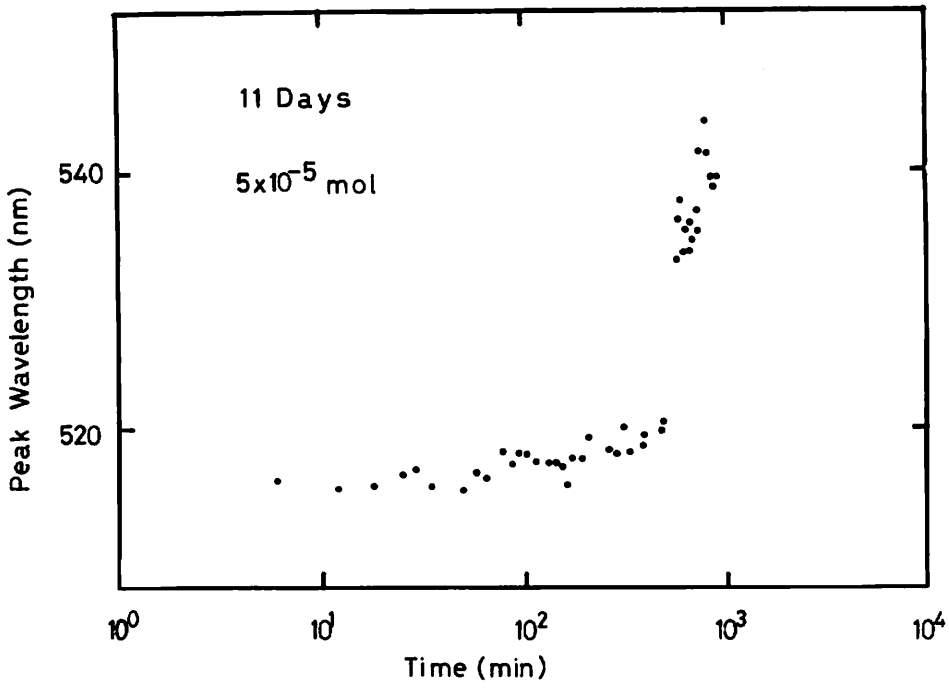

Fig. 7 Peak wavelength versus period of desiccate. The peak wavelength increases slowly and unsteadily until the gel reaches equilibrium. After equilibrium is reached, the peak wavelength begins to increase suddenly.

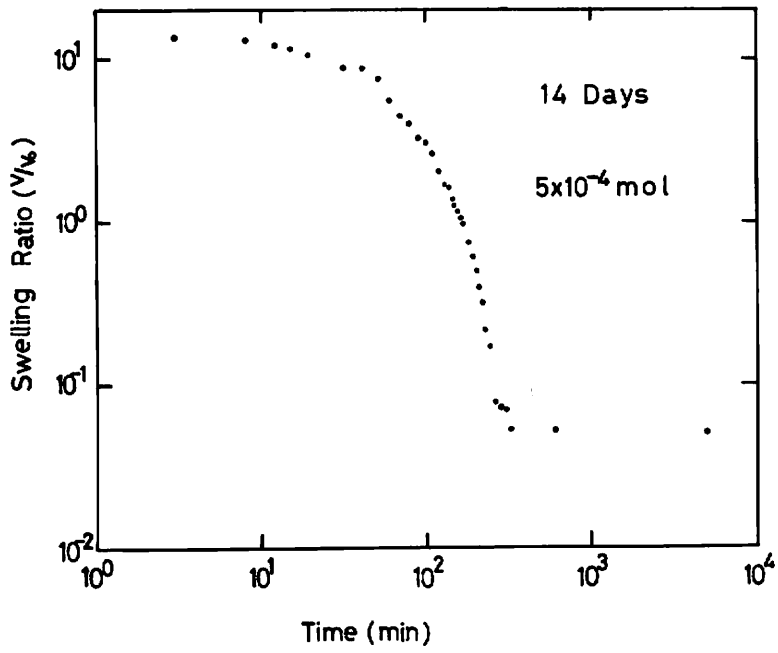

Fig. 8 Swelling curve versus period of desiccate for a gel hydrolyzed for 14 days and immersed in a 5×10^{-4} mol dye solution. The rate of volume collapse increase with time and the factor of collapse is about 250 times.

solvents (Ethanol and water with NaOH), the fluorescent band did not appear. The degree of changes of the half-width and the peak-shift of the sample are shown in Figures 6, 7. Both half-width and peak-shift increase with the collapse of gel, and their changes are slow until the gel reaches to equilibrium. But after the collapse of the gel has stopped, they both suddenly begin to increase. Some large values (range of 650 - 950 Å) of the half-width result from the appearance of the fluorescence in the wavelength range of 400 - 500 nm.

Figure 8 shows the degree of volume-collapse for a gel hydrolyzed for 14 days and immersed in 5×10^{-4} mol dye solution. The change is similar to that of the previous sample, and the degree of volume collapse is about 250-fold. Collapse has stopped at about 300 min. Figure 9 shows the fluorescence spectra of the sample at various stages of desiccation. The spectra of initial desiccation are also similar to that of the fluorescein in solvent. Fluorescence in the wavelength range 400 - 500 nm also appears on this sample, but it is hard to recognize because of its weak intensity. Figures 10 and 11 show half-width and peak-shift as a function of the swelling ratio of volume. The changes of both half-width and peak-shift are similar to that of the previous sample, but the degree of change is larger.

We also discuss an asymmetric spectral shape of the $S_1 - S_0$ transition line. We wish to suggest a model to explain this spectral shape in terms of crystal-field (17-20). Suppose that a crystal-field component mixes the S_0 state and some higher level with energy W above the

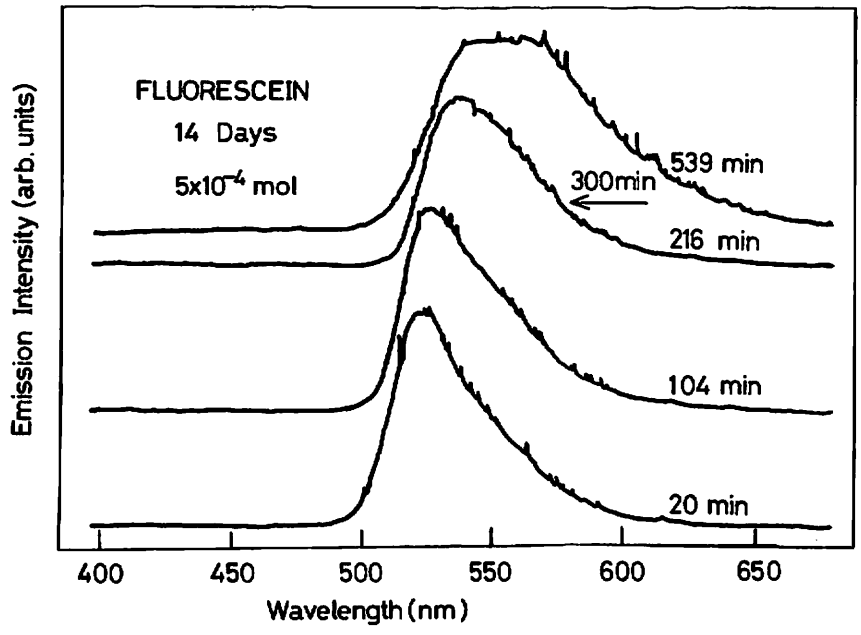

Fig. 9 Fluorescence spectra at various stages of desiccation. It is clearly observed the changing of half width and peak wavelength. Fluorescence in the wavelength range 400–500 nm is very weak compared with that of the former sample (5×10^{-5} mol).

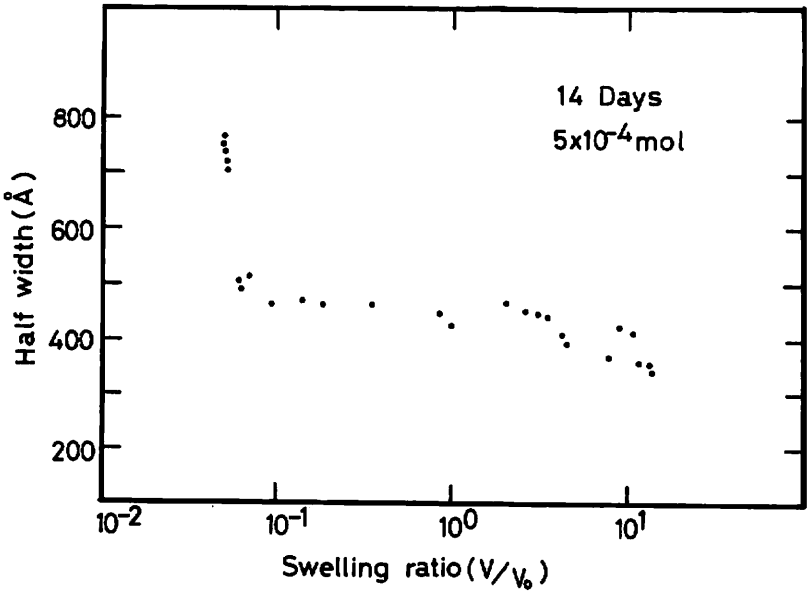

Fig. 10 Half width change as a function of swollen ratio. The change is similar to that of the former sample (5×10^{-5} mol).

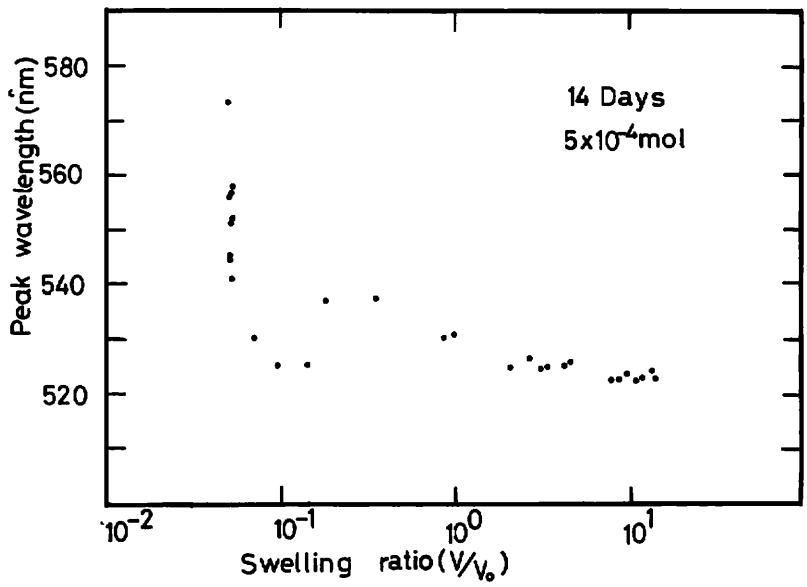

Fig. 11 Peak wavelength as a function of swelling ratio. The change is similar to that of the former sample.

ground state (S_0). Then, the S_0 state is pushed downwards by an energy E, where E(E+W) is proportional to the crystal-field strength.

If we assume that the distribution of the strength of electric field acting on the dye molecule follows a Gaussian distribution in the gel, the spectral shape for the S_1 - S_0 transition may be given by (16)

$$f(\nu) = \exp\left[-\left(\sqrt{a(\nu - \nu_0)^2 + (\nu - \nu_0) + b} - \sqrt{b} \right)^2 / c^2 \right] \quad (1)$$

where ν is the frequency with ν_0 at the line peak, and a, b and c are constant parameters.

Using the energy decrease E_0 of the S_0 state for the most probable crystal field, i.e. at the line peak, we have $a = h/(2E_0 + W)$ and $b = E_0(E_0 + W)/h(2E_0 + W)$, where h is planck's constant. Since W is consistently much larger than E_0, we may neglect the quadratic term in the square root in the equation. The agreement between the experimental fluorescence spectral shape of fluorescein dye in gel and equation (1) is quite satisfactory (17-20). Therefore, we may conclude that the wave-function mixing by a crystal field with Gaussian distribution is the origin of the asymmetric inhomogeneous broadening of this line. This result also suggests that the distribution of the environment of the doped dye is almost random in this gel system.

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