# Anomalous velocity change of surface wave near the gelation point

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## Abstract

We studied the properties of surface waves during the gelation process of tungstic acid and gelatin and silica gel by the time resolved surface wave measurements. The anomaly is clearly shown in the change of the wave number exponent $x$ ($\omega \sim k^x$, the values 1.5 and 1.0 indicate surface tension and elastic wave, respectively). $x$ of the tungstic acid was about 1.4 in the sol state and rapidly decreased to 1.0 at the gelation point. $x$ of gelatin was about 1.4 (same as tungstic acid) in the sol state and decreased gradually after the gelation point. On the other hand, $x$ of silica gel remained near 1.5 after the gelation point. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Surface wave; Gelation process; Viscoelasticity

## 1. Introduction

Tungstic acid, a kind of transition metal hydroxide, is known to exhibit electrochromism and photochromism [1–4]. Due to such properties, tungstic acid is expected to be used as display devices or shading devices activated by sunlight or applied current. From the standpoint of manufacturing, tungstic acid is most promising for inexpensive fabrication of large devices by using a sol–gel method. However, although the properties of the products have been investigated in these circumstances [5], there are only a few experimental studies on the gel structure of tungstic acid and its formation process [6–9]. Therefore, we have studied the gelation process of tungstic acid by time resolved surface wave measurements [10–12]. The properties of surface waves reflect the dynamical shear elasticity at high sensitivity [10–14], and the measurements can be performed with both liquid and solid samples.

There are some theoretical studies of surface waves on gels [15–17]. Fig. 1 shows a surface mode diagram for gels, which shows the region of capillary (surface tension), Rayleigh (elastic), overdamped and gravity modes as a function of wave number $k$ and elastic modulus $E_0$. Due to the fact that the gelation process occurs in a nonequilibrium system, this diagram cannot be applied in the strict sense. However, since this diagram is based

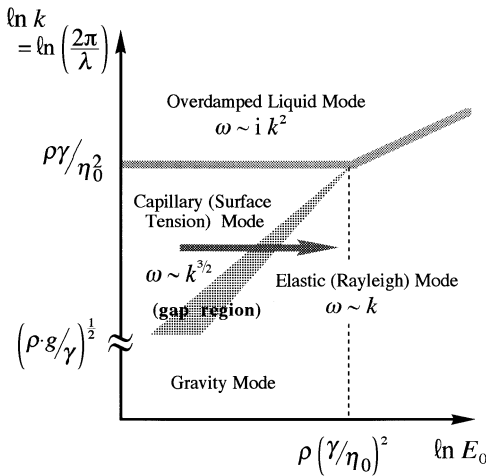*Corresponding author: Fax: +81-92-633-6958; e-mail: okabetap@mbox.nc.kyushu-u.ac.jp.

Fig. 1. Surface mode diagram for gels as a function of the wave number $k$ and elastic modulus $E_0$, where $\gamma$, $\rho$ and $\eta_0$ are the density and the surface tension of the gel and the viscosity of the solvent, respectively. The arrow at the center of the figure shows the change of elasticity during the gelation process.

only on the simple model of viscoelasticity and not on the detailed structure, we may assume that the progress of gelation is the same as the increase of the elastic modulus indicated by the arrow in the center of Fig. 1.

Our experimental results agree generally with this diagram [12]. Near the sol–gel transition point of tungstic acid, we found interesting features in the time variation of the velocities. Namely, the velocities of the surface waves having a maximum near the gelation point, decreased once rapidly, and again increased gradually as the gelation proceeded. The anomaly is clearly shown in the time dependence of the wave number exponent $x$ ($\omega \sim k^x$), too. $x$ of tungstic acid was about 1.4 (the values 1.5 and 1.0 indicate surface tension and elastic wave, respectively) in the sol state and rapidly decreased to 1.0 at the gelation time. Nakanishi et al. [16,17] had tried to explain this anomalous velocity changes by a detailed calculation with the viscoelastic model. As shown in Fig. 1, they found a gap region between the region of capillary mode and elastic mode. In the gap region, there is no solution of the wave equation localized at the surface. They supposed that this anomaly is caused by the gap region.

Therefore, further investigations are necessary to clarify the mechanism of this particular property, and we have measured the properties of surface waves and the viscoelasticity of the gelatin samples [12], which is a well-known gel and has been experimentally investigated by several researchers [14]. However, we couldn't find an anomaly like in tungstic acid. In this paper, we have tried to observe the gelation processes of silica gel, which is a colloidal gel like tungstic acid.

## 2. Experimental

The samples used were tungstic acid, gelatin and silica gel. Sample sols of tungstic acid and gelatin were prepared in the manner as described in a previous paper [12]. The sample of silica gel was prepared from tetramethyl orthosilicate (tetramethoxysilane, $Si(OCH_3)_4$; Kishida Chemical) and water (with concentration 10 vol% 20 ml/200 ml). The gelation was initiated by the mixing of tetramethyl orthosilicate and water [18].

Fig. 2 shows the improved two-point surface-wave-measurement system constructed in our laboratory [12]. In the measurement, the samples prepared in the manner described above were
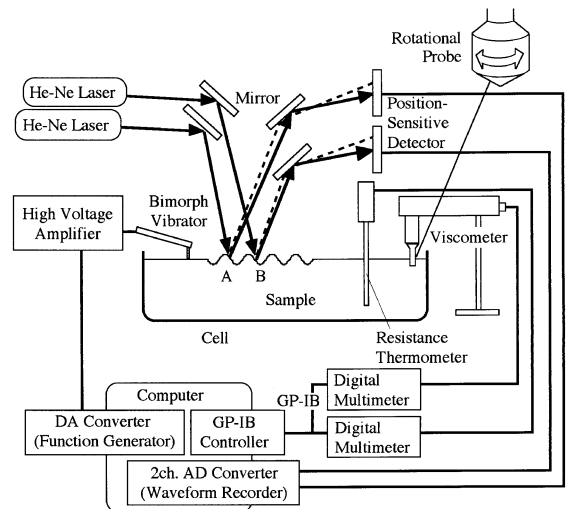


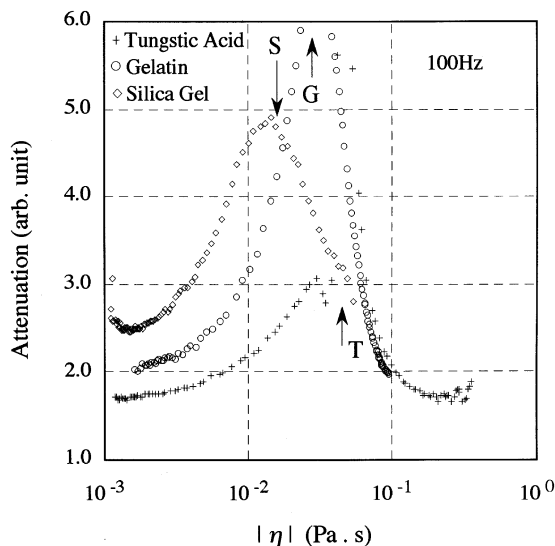Fig. 2. Schematic diagram of surface wave and viscoelasticity measuring system.

Fig. 3. Attenuation (ratio of amplitude between points A and B in Fig. 1) versus absolute value of complex viscosity $|\eta|$. The arrows indicate the gelation points.



Fig. 4. Velocity versus absolute value of complex viscosity $|\eta|$.

## 3. Results and discussion

Fig. 3 shows the attenuation (ratio of amplitude between points A and B as shown in Fig. 2) versus absolute value of complex viscosity $|\eta|$. As shown in Fig. 3, all samples showed the maximum attenuation at the $|\eta|$ range between $10^{-2}$ and $10^{-1}$ Pa.s. The arrows indicate the points of the maximum attenuation. Due to the correspondence to the titling test (the gelation point is defined at the time when the sample tilts with its vessel by the disappearance of its fluidity), we treated the points of maximum attenuation as the gelation points in the following description [11]. In sol states, the attenuation of silica gel was largest, and that of the tungstic acid gel was smallest. At the gelation point, the gelatin showed largest attenuation.

Fig. 4 shows the changes of surface wave velocities. The anomalous discontinuous velocity curve of the tungstic acid attracts attention. The velocity curves of gelatin and silica gel did not show such discontinuity, and the velocities just decreased slightly near the gelation points. However, it is noticed that the velocity values of gelatin and silica gel around the gelation points are between the values in the sol and the gel of tungstic acid. This fact probably suggests that the network in tungstic

poured into a cell. A glass tip attached to the edge of a PZT bimorph vibrator was set so as to touch the sample surface at the center of the cell. To excite the surface wave, a wave train that consists of six sine waves (50, 100, 150, 200 Hz) was applied to the bimorph vibrator. The waves propagating on the surface of the sol or gel were measured using the optical deflection method [10–13]. The distance between the two laser-beam spots was about 2 mm (distance from the vibrating tip to the first detection point was $\sim 7.5$ mm, and $\sim 9.5$ mm to the second point). The signals detected by the position sensitive detectors were recorded by an analog-digital converter board in a computer. The transit time of the surface wave was calculated by the peak time of correlation function between two waveforms. At every measurement, we measured the transit time of a wave train on water to calculate the exact value of the distance between two points. Furthermore, the absolute value of complex viscosity was measured simultaneously by means of a torsion type viscometer (Yamaichi denki Co., Ltd. VM1A-L: to be exact, the rotational resistivity measuring apparatus with the cylindrical probe).
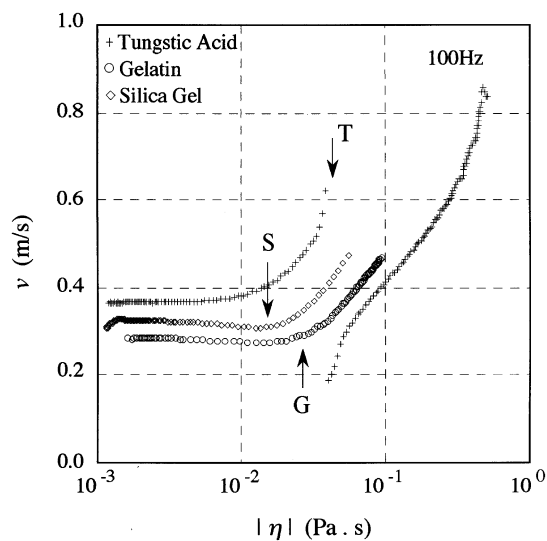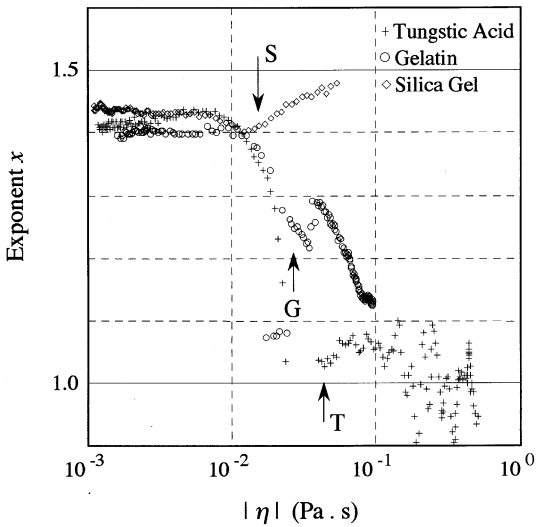
Fig. 5. Wave number exponent $x$ in the dispersion relation $\omega \sim k^x$ ($\omega$ is angular frequency) versus absolute value of complex viscosity $|\eta|$.

acid grows more uniformly than that of gelatin and silica gel and the gelation occurs more drastically.

At the gelation points, the value of $|\eta|$ of tungstic acid is largest and this property may be due to the larger elasticity of tungstic acid. For more precise discussion, we should measure the shear modulus instead of the absolute value of the complex viscosity (The reason for measuring the absolute value of the complex viscosity instead of the shear modulus was the restriction of our experimental apparatus.) An exponent $x$ of the wave number ($\omega \sim k^x$) reflects the properties of surface waves. The values of exponent $x$ of the surface tension wave and Rayleigh wave are 1.5 and 1.0, respectively. Fig. 5 shows $|\eta|$ dependence of $x$, that was calculated by using the dispersion from 50 Hz to 200 Hz.

In lower range of $|\eta|$, the values of $x$ of all samples were about 1.4. The frequency dispersion of tungstic acid above the gelation point disappeared suddenly, and the surface wave changed drastically from the surface tension wave to the Rayleigh wave at the gelation point. On the other hand, the frequency dispersion of gelatin and silica gel remained above the gelation points. The value of $x$ of gelatin decreased gradually above the gelation point. As gelation progressed and $|\eta|$ increased, it approached a value of about 1.2–1.3 at the gelation point. On

the other hand, the value of $x$ of the silica gel remained near 1.5 above the gelation point, and the surface wave on silica gel was just a surface tension wave. This may be due to the weak coupling between the network of the silica gel and the solvent. The viscoelastic theories assume the 'infinite coupling limit', but the silica gel is possibly an exception.

As described above, the quick changes of the velocity and the exponent near the gelation point of tungstic acid cannot be explained, and further investigations are necessary to clarify the mechanism of this particular property of tungstic acid. So, we will try to measure the change in the real elastic modulus near the gelation point by means of an improved viscometer. If we have achieved the measurement, we can compare the results with the theories qualitatively. And we plan to measure the properties of the other gels. For example, the vanadic acid, a kind of transition metal hydroxide may be up for the first sample.

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