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DYNAMIC PROPERTIES OF CONCENTRATED SUSPENSIONS OF CHARGED POLYSTYRENE SPHERES

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Ordered structure formation of charged polystyrene spheres was studied by measuring the order-disorder phase diagrams as well as the mechanical properties. The phase diagrams indicate that the ordering of polystyrene spheres obeys Lindemann's law of crystal melting, in which the Lindemann's parameter is about 5%. The rigidity of about 10^3 dyn/cm^2 was observed in the ordered suspension of polystyrene spheres as measured by a torsional quartz crystal method. The steady flow properties of suspensions of polystyrene spheres showed a remarkable change from a Bingham body to a Newtonian liquid at the transition point. The limit of elasticity in the ordered phase was about 1 dyn/cm^2. The viscosity in the disordered phase was well explained by the free volume theory of liquids. It is concluded from these facts that the ordered phase of polystyrene spheres is a real "crystal" whereas the disordered phase is a "liquid". Properties of ordered structures in biological systems are also discussed.

1. Introduction

Biological systems are concentrated suspensions of particles, filaments and membranes which are more or less charged, and these biological elements often make regular arrangements like crystals or liquid crystals. The semimicroscopic ordered structures in biological systems may be classified according to their symmetry [1]. First, globular proteins and viruses show three dimensional lattice structures [2–4]. Second, filaments such as muscle fibers and microtubules are packed in a hexagonal array [5]. Third, proteins in biological membranes sometimes display two dimensional crystalline structures [6]. Forth, one dimensional stacking of membranes is also found. Although these ordered arrangements are common occurrence in biological systems, the mechanism of ordering and various properties of the ordered structures are not clear enough.

The concentrated suspensions of charged polystyrene spheres, i.e. monodisperse latexes, are very similar to globular particles in biological systems such as proteins and viruses, because polystyrene spheres have considerable amount of negative surface charge and their size is very uniform. Furthermore, it has been well known that concentrated polystyrene spheres show an ordered crystalline structure of face-centered-cubic type when the volume fraction is sufficiently large and the salt concentration in the solvent is small [7,8]. Therefore, the ordered array of charged polystyrene spheres has to be a good model of ordered structures in biological systems, particularly of three dimensional lattice of particles. In the present work we have determined the order-disorder phase diagrams of the concentrated suspensions of charged polystyrene spheres with various surface charge density and measured their mechanical properties as varying the volume fraction as well as the salt concentration. The ordering mechanism and the properties of the ordered structures in biological systems are discussed on the basis of the experimental results of the latexes.

2. Phase diagrams

The order-disorder phase diagrams are shown in fig. 1 for three suspensions of polystyrene spheres whose characteristics are listed in table 1. The ordered phase appears at higher volume fraction and lower salt concentration, which is consistent with the phase diagrams by Hachisu et al. [8] and Fujita and Ametani [9]. When the surface charge is decreased, the ordered phase becomes less stable.

The qualitative feature of the phase diagrams and the dependence on the surface charge density may be

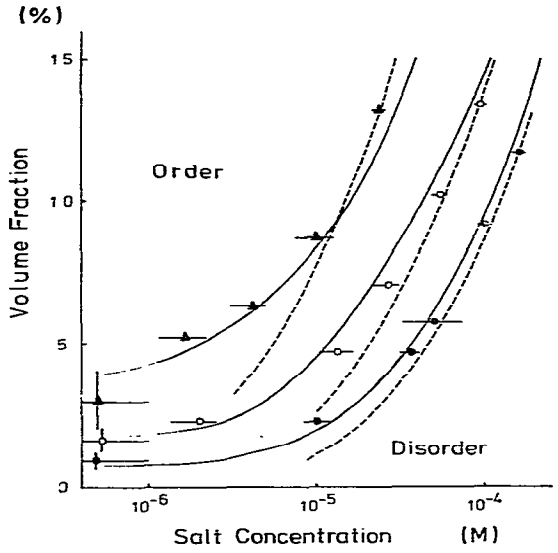

Fig. 1. Phase diagrams of the suspensions of polystyrene spheres; #1 (●), #2 (○) and #3 (▲). Solid lines and broken lines are theoretical curves by use of the Poisson–Boltzmann equation and Debye–Hückel approximation, respectively.

interpreted in terms of the schematic diagram in fig. 2. Polystyrene spheres have negative surface charges, and the counterions as well as added salts form an electric double layer. Since van der Waals attractive force is negligibly small at the interparticle distance of about 230 nm, polystyrene spheres have to be interacting only by the electrostatic repulsion. When the repulsion between particles is sufficiently large in high particle concentration and low ionic concentration regions, each polystyrene sphere is confined to the minimum of the potential valley, as shown in fig. 2. Thus, polystyrene spheres with higher surface charge density form more stable crystalline structures.

Two kinds of theories have been proposed for the explanation of the phase diagram. One is to approximate the electrostatic repulsive potential by a hard core potential [10]. In this case, the effective volume fraction ϕ^* of spheres is assumed to be described by the actual volume fraction ϕ and the Debye length $1/\kappa$ as,

$$\phi^* = \phi(1 + \lambda/\kappa a)^3 , \qquad (1)$$

where a is the radius of a sphere and λ is a constant. According to the computor experiments by Alder et al. [11], rigid spheres undergo a phase transition from a disordered phase to an ordered crystalline phase at the volume fraction of 0.5. Therefore, if we adjust the parameter λ appropriately, the phase boundary may be determined by the equation, $\phi^* = 0.5$. The dashed lines in fig. 1 are calculated in this way, in which $\lambda = 1.64$, 1.38 and 0.78 for the samples #1, #2 and #3, respectively. Although the agreement becomes worse in the low ionic concentration range due to the inapplicability of the Debye–Hückel approximation, the effective volume fraction of eq. (1) seems to represents the interaction between spheres fairly well at least in the larger ionic concentration regions. This approximation is useful for the analysis of the mechanical properties because of its simplicity.

Table 1
Characteristics of polystyrene spheres

Sample	Diameter (nm)	Dispersion (nm)	Charge (e/particle)
#1	125	5	1240
#2	159	9	810
#3	174	9	370

The other approach to the phase diagram is a more precise one, in which Lindemann's law of crystal melting is applied [12]. The electrostatic potential around a particle is calculated by solving the Poisson–Boltzmann equation numerically with an eccentric cell model. Then the phase diagram is calculated from Lindemann's

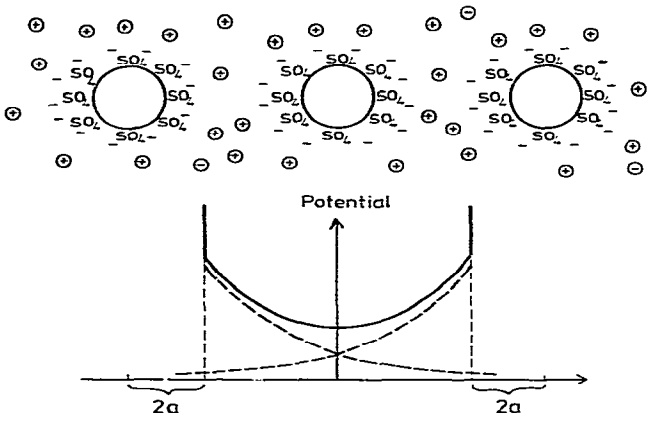

Fig. 2. Schematic diagram of polystyrene spheres and their electrostatic repulsive potential.

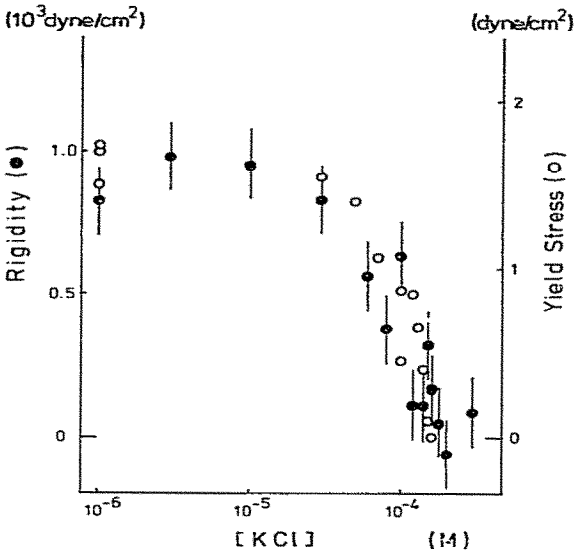

Fig. 3. Salt concentration dependence of the rigidity (●) at 40 kHz and the yield stress (○) in the ordered phase.

law,

$$\langle \delta^2 \rangle^{1/2} \sim \alpha d \,, \qquad (2)$$

in which δ is the thermal fluctuation of a particle in the effective potential valley, d is the lattice constant and α is the Lindemann's parameter which is nearly equal to 0.1. The solid lines in fig. 1 is the calculated phase boundaries, in which $\alpha = 0.05$, 0.039 and 0.04 for the samples #1, #2 and #3, respectively. The agreement between the theoretical and experimental phase diagrams is very good, and the ordered structures of polystyrene spheres melt when the thermal fluctuation of a sphere becomes larger than about five percent of the lattice constant. Consequently, the order-disorder transition of polystyrene spheres is quite analogous to the melting of crystalline solids.

3. Mechanical properties

We have measured the viscoelasticity at 40 kHz and the steady flow behaviours of the suspensions of the polystyrene spheres #1, passing through the phase transition. A torsional quartz crystal method was improved for the measurements of the viscoelasticity in aqueous suspensions, and the accuracy of ± 60 dyn/cm^2 was obtained [13]. A concentric cylinder viscometer was used for the study of the steady flow behaviours, in which the shear stress was varied from 10^{-3} to 2 dyn/cm^2 and the rate of shear could be detected in the range between 5×10^{-5} and 60 s^{-1} [14].

There was a marked change in the viscoelasticity as well as the flow properties when the salt concentration in the suspension of 11.7% was varied. Flow curves indicated that the ordered phase of polystyrene spheres is a Bingham body with a finite yield stress whereas the disordered latex is a newtonian liquid. Corresponding to this remarkable change in the flow properties, the rigidity in the ordered phase as measured by the torsional quartz crystal method sharply decreased at the transition regions.

The rigidity at 40 kHz as well as the yield stress are shown in fig. 3 as a function of the salt concentration. The rigidity is about 10^3 dyn/cm^2 at low salt concentrations and vanishes above 160 μM where the latex is in the disordered phase. The yield stress is 1.7 dyn/cm^2 below 50 μM KCl and shows the salt concentration dependence quite similar to the rigidity. Therefore, the following relationship between the rigidity G and the yield stress σ is derived,

$$\sigma = AG \,. \qquad (3)$$

Here, A is a constant independent of the concentration of the added salt and equal to 1.7×10^{-3} in the sample #1.

The finite yield stress and rigidity indicate that the crystalline array of polystyrene spheres is a real crystal in view of the mechanical properties, although the lattice constant and the nature of the interparticle potential are greatly different from those of ordinary crystals. In addition, the same relation as eq. (3) is already established for crystalline solids and has been explained by the existence and the movement of dislocations in crystallites. The validity of the same proportionality suggests that the ordered latex also undergoes a plastic deformation due to the movement of dislocations.

Although the finite rigidity in the ordered latex qualitatively indicates that it is a real crystal, the value of 10^3 dyn/cm^2 is very small as compared to the rigidity of crystalline solids, $10^{10} \sim 10^{12}$ dyn/cm^2. However, this disagremeent may be reasonably explained by the following estimation. The order of magnitude of the modulus M of crystals may be written by the magnitude of the thermal fluctuation δ of a particle as,

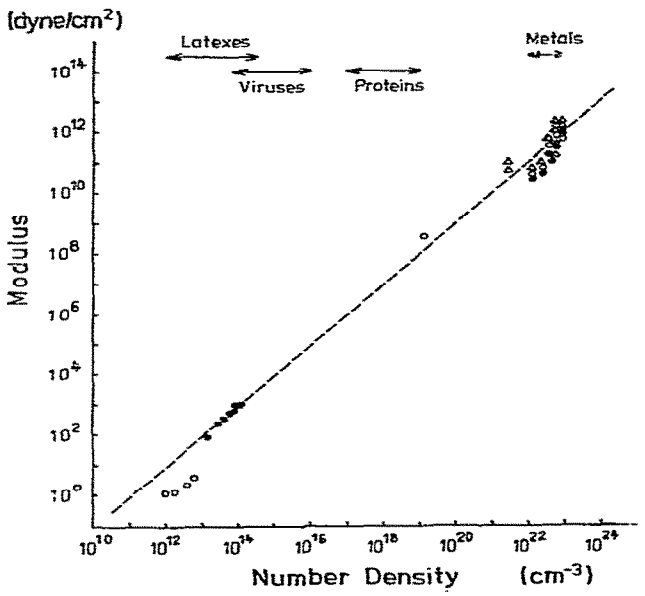

Fig. 4. Moduli of various crystalline structures are plotted as a function of the number density of molecules or particles. A broken line represents the equation, $M = NkT/\beta^2$, in which $1/\beta^2$ is assumed to be 10^3.

$$M \sim f/d \sim kT/\langle\delta^2\rangle d\,, \tag{4}$$

where f is the force constant and kT is the thermal energy. If we substitute a nondimensional parameter β for $\langle\delta^2\rangle^{1/2}/d$, M is obtained as a linear function of the number density N of a particle,

$$M \sim NkT/\beta^2\,. \tag{5}$$

Since $\beta < \alpha \sim 0.1$ for stable crystals due to the Lindemann's law of eq. (2), it should be reasonable to assume that $1/\beta^2 \sim 10^3$ in crystals of metals as well as latexes. Fig. 4 shows the moduli of ordered polystyrene spheres together with metals and the dashed line represents eq. (5) on the assumption that $1/\beta^2 \sim 10^3$. The agreement of eq. (5) with experimental values is fairly good, and it may be concluded that the difference in the magnitude of the rigidity between the ordered polystyrene spheres and metal crystals is mainly due to the difference in the number density of these systems. The moduli is a kind of energy density and the moduli of protein or virus crystals are also expected to be estimated by eq. (5).

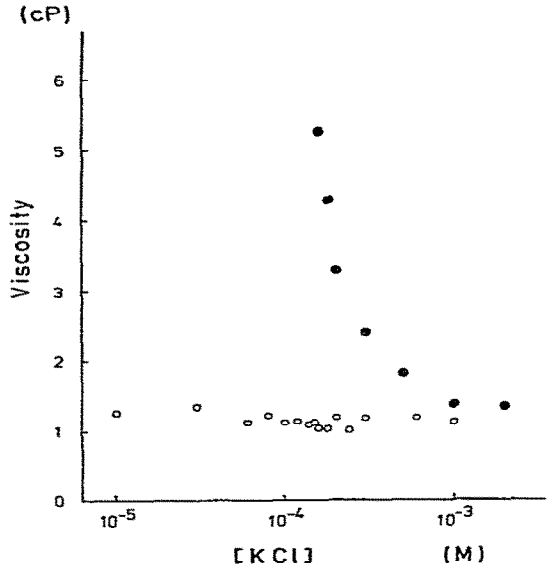

Fig. 5. Salt concentration dependence of the steady flow viscosity as well as the dynamic viscosity at 40 kHz in the disordered phase.

In contrast to the ordered state, the disordered state of polystyrene spheres showed a Newtonian flow curve. Fig. 5 shows the salt concentration dependence of the steady flow viscosity together with the dynamic viscosity at 40 kHz. The steady flow viscosity increases divergently in the vicinity of the melting point, and the yield stress appears at the melting point. On the other hand, the dynamic viscosity is much smaller than the steady flow viscosity and does not have any singularity at the melting point.

At present, there is no exact theory of suspension viscosity dealing with the strong electrostatic interaction between particles. But we have already elucidated that the ordered structure of latex is a crystal, and therefore the disordered state is expected to be a liquid. Now we try to explain the distinct salt concentration dependence of the steady flow viscosity by the free volume theory of the transport phenomena in liquids and glasses [15]. Cohen and Turnbull have assumed that the diffusion of a molecule in liquids occurs when the free volume exceeds some critical value. Calculating the statistical redistribution of the free volume, the diffusion constant of the molecule has been determined in terms of the probability of the free volume larger

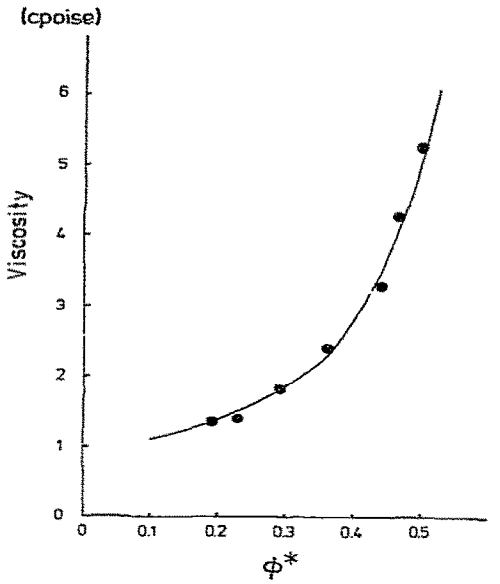

Fig. 6. The steady flow viscosity is replotted against the effective volume fraction. A solid line represents the theoretical curve.

than the critical value. We have applied this concept to the case of the disordered polystyrene spheres which are strongly interacting with each other by the electrostatic repulsion and obtained the following expression of the diffusion constant [16].

$$D = D_0 \exp\left(-\frac{2.82\gamma\phi^*}{1-\phi^*}\right), \tag{6}$$

in which ϕ^* is the effective volume fraction which is defined by eq. (1), D_0 is the diffusion constant of a particle in water and γ is a constant in the range from 0.5 to 1. Since the viscosity is described by

$$\eta \sim G_g \tau \sim G_g d^2/D\,, \tag{7}$$

we obtain

$$\eta = \frac{G_g d^2}{D_0} \exp\left(\frac{2.82\gamma\phi^*}{1-\phi^*}\right), \tag{8}$$

where G_g is the glass-like rigidity at high frequencies and τ is the relaxation time of the glass-like state. The best fitted curve is shown in fig. 6, in which $G_g d^2/D_0 = 0.0091$ and $2.82\gamma = 1.70$. Since the relaxation time τ has to be longer than d^2/D_0 which is roughly estimated from $d \sim 10^{-5}$ cm and $D_0 = kT/6\pi\eta a \sim 10^{-7}$ cm^2 s^{-1} to be about 10^{-3} s, the frequency of 40 kHz is high enough to measure the glass-like state. Therefore, the decrease in the viscosity at 40 kHz as compared to the steady flow viscosity is due to the freezing of the movement of particles. We have previously found that the rigidity of $0 \sim 10^2$ dyn/cm^2 is observed at 40 kHz in the disordered state [17]. Substituting this value. $G \sim 10$ dyn/cm^2, with $d^2/D_0 \sim 10^{-3}$, $G_g d^2/D_0$ is calculated as 0.01 which is in good agreement with experimental value. The value of γ, 0.60, is also reasonable. Thus, the disordered latex appears to be understood as a liquid of polystyrene spheres interacting with electrostatic repulsion.

4. Discussion

Experimental results for the suspensions of charged polystyrene spheres are as follows,

(1) The ordered structure of polystyrene spheres is formed by an electrostatic repulsion between spheres.

(2) The order-disorder transition obey's Lindemann's law of crystal melting.

(3) Finite rigidity and yield stress was measured in the ordered state indicating that the ordered latex is a real crystal, and the relationship between them indicates a dislocation mechanism of the plastic deformation.

(4) The steady flow viscosity in the disordered state was reasonably explained by the free volume theory of liquids.

One of the most important conclusion in the present work is that the ordered structure of charged spheres may be formed by the purely repulsive electrostatic interaction between spheres which are confined in a limited volume of the solvent. Consequently there may be at least three kinds of ordered structures in biological systems with respect to the dominant pair interaction between particles or filaments; the electrostatic repulsion, the van der Waals attraction and some more specific interactions. When the electrostatic repulsion is dominant, the particles have to be in a limited volume surrounded by some membranes or organellas for the formation of lattice structures. On the other hand, crystalline structures are formed spontaneously, when the van der Waals attraction is dominant. Examples of these ordered structures are the following. Some crystalline arrays of spherical viruses [2] and the two dimen-

sional lattice of muscle filaments [18] are primarily formed by the repulsive interaction. Crystals of globular proteins appears to be formed spontaneously due to the van der Waals attraction [19]. More specific interaction is expected in some globular protein assemblies like F-actin [20].

The ordered structure formed by the repulsion has more flexibility of various characteristics than other types of ordered structures. Namely, the lattice constant does not depend on the strength of the interaction but is inversely proportional to the cubic root of the volume fraction of spheres or the square root of the concentration of filaments. The melting of the ordered structures may easily occur due to the changes in the volume fraction, salt concentration and pH. Because of these flexible natures, the ordered structure formed by the repulsive interaction appears to be more suitable for biological systems in some cases than other types of ordered structures.

Another important result of this work is the fact that the three dimensional ordered structure of charged spheres is essentially the same as ordinary crystalline solids in their melting behaviours as well as the mechanical properties. Therefore, it should be reasonable to assume that the three dimensional lattice in biological systems also has the same properties. That is, they will obey Lindemann's law and have the finite rigidity and yield stress which is determined by eqs. (3) and (5). We will present in a forthcomming paper the detailed description of the mechanism of ordering and the mechanical properties of some lattice structures in biological systems.

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