Biophysical Chemistry 14 (1981) 45–53
Elsevier/North-Holland Biomedical Press

DIELECTRIC PROPERTIES OF SPHERICAL MACROION SUSPENSIONS
I. STUDY ON MONODISPERSE POLYSTYRENE LATEX

Shigeo SASAKI
Department of Physics, Faculty of Science, Nagoya University, Nagoya 464, Japan

and

Akira ISHIKAWA and Tetsuya HANAI
The Institute for Chemical Research, Kyoto University, Uji 611, Japan

Received 3 September 1980
Revised manuscript received 4 March 1981

Dielectric properties of polystyrene latex suspended in aqueous media are investigated with special attention to the effect of volume fraction of the latex and salt concentration. The experimental data show the existence of two dispersions, one in the low-frequency range from 10^3 to 10^5 Hz, and the other in the high-frequency range from 10^5 to 10^7 Hz. In the salt-free system, both dispersions are of the Debye type and their relaxation times are insensitive to the volume fraction. Addition of H_2SO_4 to the suspension enlarges the magnitude of the low-frequency dispersion and reduces that of the high-frequency dispersion, whereas it does not affect the relaxation times. In the mixture of two species of counterions, e.g. H^+ and Na^+, the low-frequency dispersion deviates from the Debye type, while the high-frequency dispersion does not. From these facts, the high- and low-frequency dispersions are thought to be due to the radial and tangential components of the displacement current at the surface of the latex. The latter process is consistent with the Schwarz theory of the dielectric dispersion of colloidal suspensions.

1. Introduction

The measurement of a dielectric dispersion of macromolecules exhibits large dielectric increments in the low-frequency region (of an ac electric field). This was first found in rod-like macroion systems such as DNA which was believed to have no molecular permanent dipole moments [1–4]. Ever since, various extensive investigations have been performed on the dielectric properties of synthetic polyelectrolytes and biological materials [5,6].

Two decades ago, Schwan et al. [7] found that the colloidal suspensions of polystyrene latex showed an extremely large dielectric increment with a dispersion frequency at several kHz. This phenomenon was explained by the concept of frequency-dependent surface-conductivity induced by the motion of bound counterions along the surface of the polyion [8,9]. Recently, several works were presented on the dielectric dispersion of the polystyrene lattices at higher frequencies, which was not found in the experiments of Schwan et al. Their work, however, showed that the dielectric increment at higher frequencies was very small and the obtained data were scattered because of the very small volume fraction (≈ 0.02) used in their experiments [10,11]. Therefore, some ambiguities still remained in the experimental results.

It is reasonably expected that a spherical macroion system such as polystyrene latex shows two dispersions: the first may be to a polarization mechanism of counterions on the surface of the polystyrene sphere, whereas the second may be to the Maxwell–Wagner effect [12]. However, to clarify the second dispersion, more accurate measurements are necessary in a wide frequency region. Besides these problems, the preparation of the latex is also important in the analysis of the experimental data. Namely, it is desirable to obtain the latex with a quite narrow particle size distribution to remove the distribution of relaxation times due to the size distribution. This requirement is almost achieved in our experiment.

In this study, the dependence of the dielectric properties at lower and higher frequencies on the volume fraction of the latex and on the salt concentration is investigated to elucidate the polarization mechanism of the latex suspensions. The effect of the coexistence of two mixed counterions, H^+ and Na^+, on the dielectric dispersion is also examined. The relaxation process is carefully analyzed by using almost monodisperse latex to clarify the distribution of the relaxation times.

2. Materials

Monodisperse polystyrene latex was synthesized by emulsion polymerization, the recipe of which is shown in table 1. The chemicals used were commercial ones and the inhibitor contained in the commercial styrene monomer was removed by NaOH aqueous solution. Redistilled water was used in the polymerization experiments. The polymerization was carried out in a 2 l three necked flask by stirring the reaction mixture. Before adding the initiator, the oxygen gas was removed from the flask by bubbling with N_2 gas for 1 h. The polymerization was continued over an atmosphere of N_2 gas for 12 h at 60°C for sample B-2 and 70°C for sample T-0, respectively. The polymerized latex was mixed with MB-3 mixed bed ion-exchange resin and stirred for deionization. The mixture of the latex and the ion-exchange resin was kept stirring for 6 h until the appearance of the iridescence. The ion-exchange resin was removed from the samples by filtration. The particle size and the number of charged groups which are strongly acidic as shown in table 1 were determined by electron microscopy and conductometric titration, respectively. On the other hand, the volume fraction, ϕ, was obtained from the weight fraction, ϕ_w, referring to the fact that the specific gravities of water and latex are 1.0 and 1.05, respectively [13]; ϕ is given by the relation $\phi = \phi_w/(1.05-0.05\ \phi_w)$. The dielectric measurements were performed within a week after deionization, so that the decomposition of the strong acid must be negligible.

The concentrations of the titrants, H_2SO_4 and NaOH, were determined by potentiometric titration. NaOH solutions of required concentration were prepared by diluting quickly the supernatant of saturated NaOH solutions, which removed Na_2CO_3 contamination in the precipitate. Several 10 μl of the H_2SO_4 (15.8 mN) or NaOH (64.2 mN) solution were added from a microburet into a cell for dielectric measurements containing 4 ml latex suspension; the change in ϕ caused by the addition of H_2SO_4 or NaOH was negligible. The iridescence did not disappear in any case in the present experimental conditions. This fact, therefore, shows the polystyrene latex suspensions have constructed an ordered structure.

Table 1

Recipes for the polymerization of latex

	Styrene (mole/l)	Na_2SO_4 (mmole/l)	NaSS a) (mmole/l)	Emulsifier (mmole/l)		Initiator (mmole/l)		Diameter (Å)	Number of charged groups
				SOS b)	SDS c)	$Na_2S_2O_8$	$K_2S_2O_8$		
B-2	2.0	12.0	4.0	0.21	0	4.0	0	1790	8280
T-0 d)	1.15	0	0	0	0.115	0	3.67	5050	–

a) NaSS. P-sodium styrene sulfonic acid.
b) SOS. sodium octadecyl sulfate.
c) SDS. sodium dodecyl sulfate.
d) pH of the polymerizing solution was adjusted to be about 10 by adding 0.1 N KOH solution.

3. Measurements and analysis

The dielectric measurements were carried out with an Ando Bridge type TR-1C covering the frequency range from 30 Hz to 1 MHz, and a Boonton R-X meter type 250 A covering the frequency range from 1 MHz to 170 MHz. A dielectric cell consisting of parallel platinum rod-like electrodes was used in our experiments.

The correction for residual inductance at high frequency was made by Schwan's method [14]. The effect of the electrode polarization at lower frequencies was eliminated in the following way. The apparent values of permittivity, ϵ_{app}, and conductivity, κ_{app}, are related to their true values in the solution, ϵ and κ, by the following semi-empirical equations [15,16],

$$\epsilon_{app} = \epsilon + C_0 z_0 \kappa^2 \sin(\tfrac{1}{2}n\pi)\omega^{-n}/\omega\epsilon_v, \qquad (1)$$

$$\kappa_{app} = \kappa - C_0 z_0 \kappa^2 \cos(\tfrac{1}{2}n\pi)\omega^{-n}, \qquad (2)$$

where ϵ_v, C_0 and z_0 are the absolute dielectric constant of free space, the cell constant, and the characteristic constant of the circuit, respectively. In the above equations, n stands for the exponent of the electrode impedance z_{el} in the assumed expression, $z_{el} = z_0(i\omega)^{-n}$. On the other hand, by use of the Cole–Cole dispersion formula [17], ϵ and κ consisting of N dispersions must be expressed as

$$\epsilon = \epsilon_h + \sum_{i=1}^{N} a_i \Delta\epsilon_i / (a_i^2 + b_i^2), \qquad (3)$$

$$\kappa = \kappa_l + \sum_{i=1}^{N} \left[b_i \Delta\epsilon_i / (a_i^2 + b_i^2) \right] \omega\epsilon_v, \qquad (4)$$

where

$$a_i = 1 + \sin(\tfrac{1}{2}\alpha_i\pi)(\omega\tau_i)^{(1-\alpha_i)}, \qquad (5)$$

$$b_i = \cos(\tfrac{1}{2}\alpha_i\pi)(\omega\tau_i)^{(1-\alpha_i)}. \qquad (6)$$

Here, ϵ_h, κ_l, $\Delta\epsilon_i$, α_i and τ_i are the limiting value of ϵ at high frequency, the limiting value of κ at low frequency, the dielectric increment, the Cole parameter and the relaxation time of the ith dispersion, respectively. Then, by combining eqs. (1)–(6), ϵ_{app} and κ_{app} are expressed as functions of the $(4+3N)$ parameters, ϵ_h, κ_l, z_0, n, $\Delta\epsilon_1$, α_1, $\tau_1, \ldots, \Delta\epsilon_N$, α_N and τ_N. The measured values of the permittivity ϵ_{meas} and the conductivity κ_{meas} are adjustable as parameters in minimizing the function F defined by

$$F = \sum_{\omega_{data}} \left\{ \left[\ln(\epsilon_{meas}/\epsilon_{app})\right]^2 + \left[\ln(\kappa_{meas}/\kappa_{app})\right]^2 \right\}, \qquad (7)$$

where $\Sigma_{\omega_{data}}$ denotes the summation over all measured frequencies. In this study, the minimization of the function, F, with $(4+3N)$ parameters was performed by using Davidon's variable metric method [18,19]. This method is commonly used in solving minimization problems of nonlinear functions, and its detailed algorithm is shown in ref. [19]. In order to check the reliability of this method, minimization of F as a function of 13 parameters $(N=3)$ was carried out for values of ϵ_{meas} and κ_{meas} which were artificially constructed by

$$\epsilon_{meas} = (1 + RE)\epsilon_{app}, \qquad (8)$$

$$\kappa_{meas} = (1 + RE)\kappa_{app}, \qquad (9)$$

Table 2

Result of the analysis of the artificially constructed data (see text)

Error data (E)		z_0 ($\times 10^5$)	ϵ_∞	κ_0 ($\mu\Omega^{-1}$ cm^{-1})	$\Delta\epsilon_1$	τ_1 ($\times 10^{-8}$)	α_1	$\Delta\epsilon_2$	τ_2 ($\times 10^{-6}$)	α_2	$\Delta\epsilon_3$	τ_3 ($\times 10^{-5}$)	α_3
0	0.8305	2.000	58.50	105.5	65.70	1.590	0.1400	200.0	1.000	0.1400	10000	1.000	0.1400
0.01	0.8306	2.004	58.41	105.3	65.67	1.592	0.1403	197.3	0.991	0.1485	1001	0.9980	0.1410
0.03	0.8305	2.009	58.23	105.0	65.48	1.592	0.1402	198.7	0.998	0.1393	995.7	0.9996	0.1399
0.05	0.8305	2.015	58.10	104.7	65.31	1.593	0.1402	196.5	0.993	0.1379	994.5	0.9983	0.1406

where R is a random number restricted to $-1 \leq R \leq 1$, and E stands for the degree of error of the measured values. The values of ϵ_{app} and κ_{app} are given by the substitution of the 13 parameters into eqs. (1)–(6). The results obtained by this method were excellent as shown in table 2.

All analyses in this study were performed by the use of a FACOM M-200 computer.

4. Results

As shown in fig. 1, the experimental data obviously indicate the existence of the two dispersions, the relaxation frequencies of which are indicated by arrows. The abrupt increase of the permittivity at lower frequencies seen in fig. 1 is due to the effect of electrode polarization. This effect was eliminated by use of Davidon's variable metric method on the assumption that the dielectric dispersion can be described by the Cole–Cole dispersion formula as illustrated in the previous section.

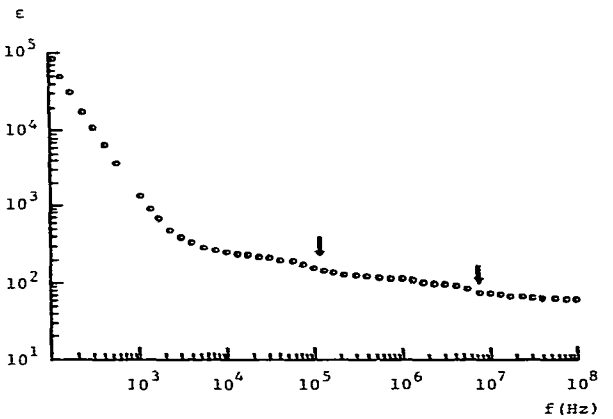

Fig. 1. Permittivity ϵ as a function of frequency for B-2 polystyrene latex suspension at $\phi = 0.1544$. The arrows indicate the dispersion frequencies.

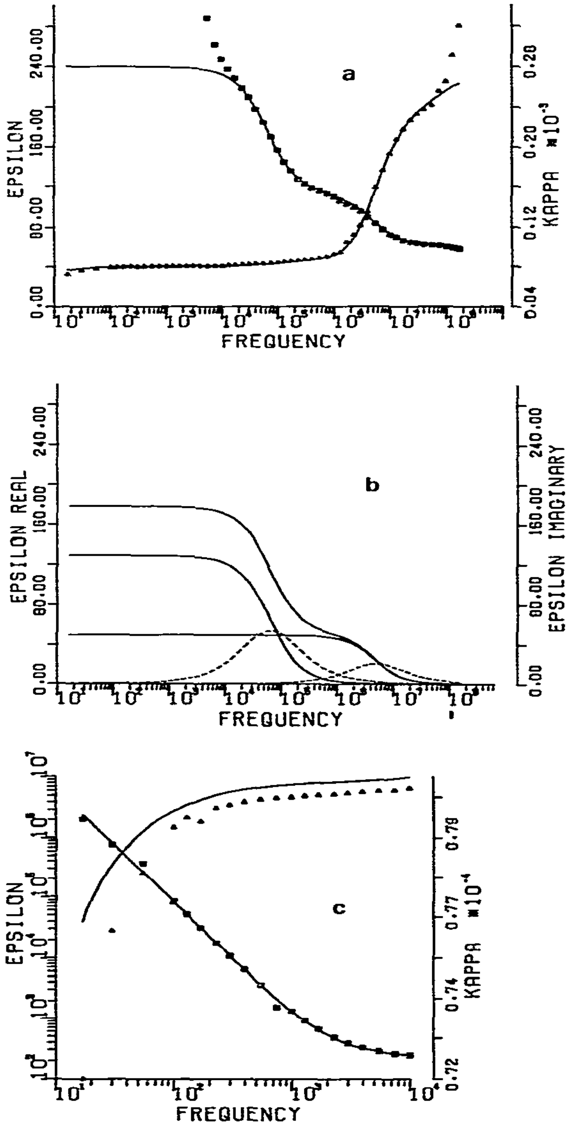

Fig. 2. Dielectric dispersion of the B-2 latex at $\phi = 0.1544$ in the absence of added acid or alkali, i.e. $R_{H^+} = 1.00$ and $r_{Na^+} = 0.00$. (a) Comparison of measured permittivity (□) and conductivity (△) with calculated values (———). The corrections for residual inductance at higher frequencies and for the polarization effect on the permittivity are made. Solid lines are the calculated values of the permittivity and conductivity. The calculation procedure is described in the text. (b) Decomposition of the dielectric dispersion curve into two dispersions. The solid and broken lines are the real and imaginary parts of the dielectric increment for the two dispersions, respectively. The uppermost solid line is the total increment. (c) The permittivity (□) and conductivity (△) in the frequency region from 10 Hz to 10 kHz. Solid lines are the calculated values corresponding to the measured ones.

The elimination of the polarization effect was satisfactorily done by assuming the existence of the two dispersions. The calculated curves for the dielectric dispersions are shown in figs. 2 and 3. The discrepancy between the calculated and experimental conductivity values was within experimental error in the low-frequency range. The abrupt increase of the conductivity at frequencies above 100 MHz is thought to be due to the insufficient correction for the residual inductance of the circuits. Therefore, the dispersions which appeared in the conductivities in the frequency region above 100 MHz were not analyzed in the present study.

Table 3 shows the dependence of ϵ_∞, κ_0, $\Delta\epsilon_l$, τ_l, α_l, $\Delta\epsilon_h$, τ_h and α_h, obtained from the analysis of the experimental data of polystyrene lattices in salt-free suspension, on the volume fraction. Since in the high-frequency limit the phase difference of the electric current is too small to observe its magnitude in the permittivity, the volume fraction dependence of ϵ_∞ in the range of volume fraction in our present experiments can be approximately described by Wiener's equation [20]

$$\epsilon_\infty = \frac{2\epsilon_m + \epsilon_p - 2\phi(\epsilon_m - \epsilon_p)}{2\epsilon_m + \epsilon_p + \phi(\epsilon_m - \epsilon_p)}\epsilon_m, \tag{10}$$

where ϵ_m, ϵ_p and ϕ are the permittivities of water and latex, and the volume fraction, respectively. In fact, the obtained value of ϵ_∞ agrees well with that predicted by eq. (10) as shown in fig. 4, when ϵ_m and ϵ_p are assumed to be 78 and 2. This fact supports the present conclusion that the dispersion appearing above 100 MHz is caused by some artifact, probably due to insufficient correction for residual inductance of the circuits as mentioned above.

The relaxation times, τ_h and τ_l, were insensitive to the volume fraction in the region $\phi < 0.15$. The fact that τ_l is independent of the volume fraction is consistent with the Schwarz theory [8]. Now, the dispersion at higher frequencies is temporarily assumed to be due to the Maxwell–Wagner effect [12], the relaxation time of which is given by

$$\tau_h = \frac{2\epsilon_m + \epsilon_p + \phi(\epsilon_m - \epsilon_p)}{2\kappa_m + \kappa_p + \phi(\kappa_m - \kappa_p)}\epsilon_v, \tag{11}$$

where κ_m and κ_p are the conductivities of water and latex, respectively. By putting $\kappa_p = 0$, $\epsilon_m = 78$ and $\epsilon_p = 2$ into eq. (11), κ_m can be obtained from the observed values of τ_h. As shown in table 4, the calculated values, κ_m, are much larger than the observed values of κ_0. This fact indicates that the dispersion at higher frequency cannot be explained simply by the Maxwell–Wagner effect.

The Cole parameters obtained from an analysis of the experimental data of the salt-free system seen in table 3 are so small that the dielectric dispersions at higher and lower frequencies can be regarded as Debye dispersions. This is due to the narrow distribution of the mobility of the counterion, which is the hydrogen ion in this case.

The effect of the addition of H_2SO_4 on the dielectric dispersion profile is shown in fig. 5. The

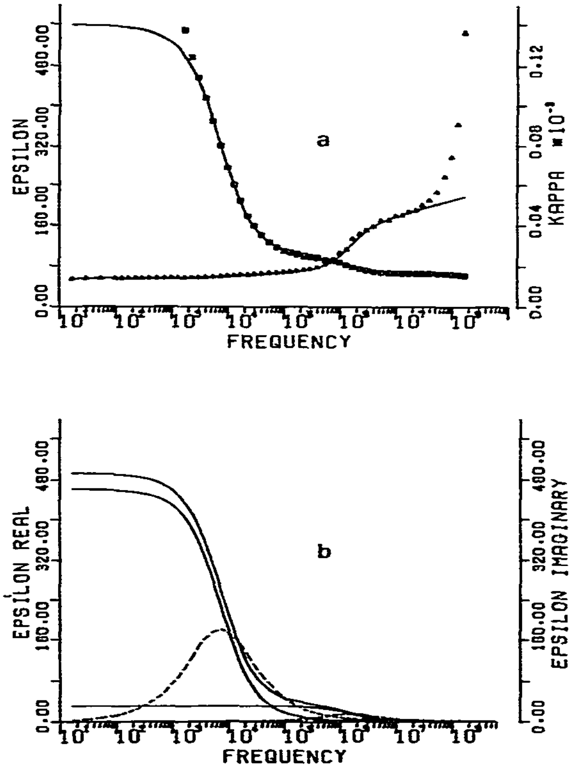

Fig. 3. (a), (b) Dielectric dispersion of the T-0 latex at $\phi = 0.1161$. Notation as in figs. 2a and 2b.

Table 3

Result of analysis of the experimental data of B-2 latex and T-0 latex

	ϕ	ϵ_∞	κ_0 ($\mu\Omega^{-1}$ cm^{-1})	$\Delta\epsilon_l$	τ_l	α_l	$\Delta\epsilon_h$	τ_h	α_h	T (°C)
B-2	0.1544	60.9	80.6	131.1	2.43×10^{-6}	0.129	48.8	3.17×10^{-8}	0.064	22.5
	0.1274	63.7	56.5	78.6	1.75×10^{-6}	0.093	47.1	4.63×10^{-8}	0.106	22.0
	0.0995	67.3	40.3	37.8	1.40×10^{-6}	0.105	38.5	4.10×10^{-8}	0.076	23.2
	0.0497	72.6	15.2	222.5	1.17×10^{-6}	0.414	18.9	4.39×10^{-8}	0.017	23.0
T-0	0.1161	64.5	14.1	463.5	2.19×10^{-5}	0.155	30.4	1.15×10^{-7}	0.069	23.8

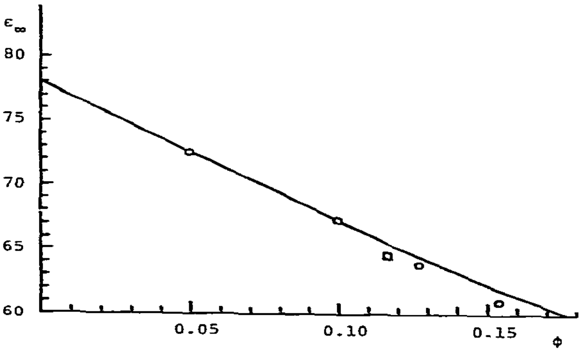

Fig. 4. Permittivity at higher-frequency limit as a function of the volume fraction. ○ and □ are measured values for B-2 and T-0 latex, respectively. The solid line is calculated by use of eq. (10).

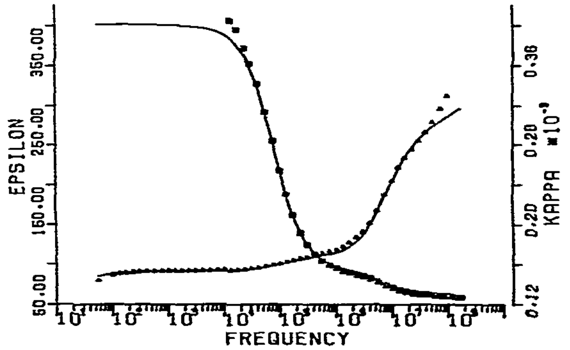

Fig. 5. Effect of the addition of H_2SO_4 on the dielectric dispersion of the B-2 latex at ϕ=0.1544 and R_{H^+}=1.335. Notation as in fig. 2a.

values of ϵ_∞, κ_0, ϵ_l, τ_l, α_l, ϵ_h, τ_h and α_h obtained by analysing these dispersion profiles are summarized in table 5. From these observed values it can be pointed out that the addition of acid reduces the dielectric increment at high frequency and enlarges the magnitude of the dielectric dispersion at low frequency. On the other hand, the relaxation times and the Cole parameters at both high and low frequencies are little affected by the addition of acid. These facts indicate that the dielectric dispersions at high and low frequencies are correlated with each other.

The effect of neutralization, i.e. the exchange of counterion from hydrogen ion, H^+, to sodium ion, Na^+, on the dielectric dispersions is shown in fig. 6, and the values of ϵ_∞, κ_0, ϵ_l, τ_l, α_l, ϵ_h, τ_h and α_h obtained from the analysis of the data are summarized in table 6. The most characteristic property of this effect is that the dispersion profile at low frequency starts to deviate from the Debye dispersion, while the dispersion profile at high frequency is of the Debye type. The broadness of the dispersion in the low-frequency region is ascribed to the existence of the broad distribution of the counterion mobility. The coexistence of two

Table 4

Comparison of the calculated values, κ_m, by use of eq. (11) with the experimental values of κ_0

ϕ	κ_m ($\mu\Omega^{-1}$ cm^{-1})	κ_0 ($\mu\Omega^{-1}$ cm^{-1})
0.154	220	80.6
0.127	151	56.5
0.0995	170	40.3
0.0497	159	15.2

Table 5

Effect of the addition of H_2SO_4 on the parameters which describe the dielectric dispersion [a)]

R_{H^+} [b)]	ϵ_∞	κ_0 ($\mu\Omega^{-1}$ cm^{-1})	$\Delta\epsilon_l$	τ_l	α_l	$\Delta\epsilon_h$	τ_h	α_h	T (°C)
1.00	60.9	80.57	131.1	2.43×10^{-6}	0.129	48.8	3.17×10^{-8}	0.064	22.5
1.11	61.6	111.2	214.9	2.14×10^{-6}	0.122	40.3	2.99×10^{-8}	0.076	22.0
1.22	61.4	131.7	258.9	2.06×10^{-6}	0.088	34.7	2.65×10^{-8}	0.076	22.4
1.335	61.0	154.0	311.2	2.00×10^{-6}	0.093	29.4	2.38×10^{-8}	0.084	23.3

[a)] These values are for the B-2 latex at $\phi=0.1544$.

[b)] R_{H^+} is the ratio of total number of counterions, H^+, to the amount of charge for a polystyrene latex.

Table 6

Effect of the exchange of the counterion from H^+ to Na^+ on the dielectric dispersion [a)]

r_{Na^+} [b)]	ϵ_∞	κ_0 ($\mu\Omega^{-1}$ cm^{-1})	$\Delta\epsilon_l$	τ_l	α_l	$\Delta\epsilon_h$	τ_h	α_h	T (°C)
0	60.9	80.57	131.1	2.43×10^{-6}	0.129	48.8	2.17×10^{-8}	0.064	22.5
0.227	62.3	59.63	102.9	2.39×10^{-6}	0.177	50.9	4.25×10^{-8}	0.089	22.0
0.454	62.2	41.83	117.7	2.49×10^{-6}	0.393	38.4	4.83×10^{-8}	0.000	22.0
0.681	62.2	26.70	83.8	2.87×10^{-6}	0.325	55.8	7.30×10^{-8}	0.080	23.5
0.908	61.9	26.60	86.1	4.77×10^{-6}	0.350	63.1	8.13×10^{-8}	0.080	23.5

[a)] These values are for the B-2 latex at $\phi=0.1544$.

[b)] r_{Na^+} is the exchange rate defined as r_{Na^+} = number of NaOH added/total amount of charge of polystyrene latex in the solution.

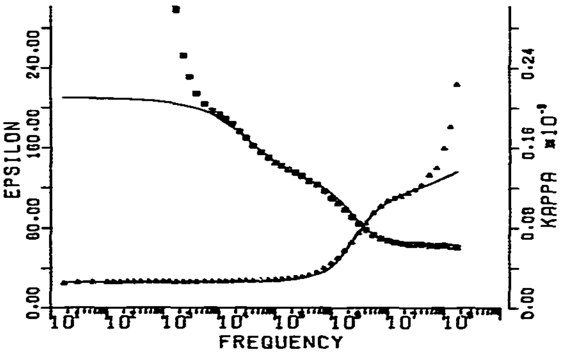

Fig. 6. Dielectric dispersion of the B-2 latex at $\phi=0.1544$ and $r_{Na^+}=0.908$. Notation as in fig. 2a.

counterion species, H^+ and Na^+, obviously broadens the distribution of the counterion mobility as a whole.

5. Discussion

The dielectric properties of the suspension of polystyrene latex observed in the present experiments can be summarized as follows. (1) Polystyrene latex suspension in a salt-free system shows two Debye-type dielectric dispersions, the relaxation times of which are insensitive to the volume fraction. (2) The addition of acid enlarges the dielectric increment on the low-frequency side, but it diminishes that on the high-frequency side. (3) In the presence of two species of counterions having different mobilities, the dispersion profile in the lower-frequency range deviates from the Debye dispersion, while the dispersion in the higher-frequency range is unaffected even when a wide distribution of counterion mobility exists.

The dielectric dispersion at lower frequencies is thought to be due to the polarization mechanism proposed by Schwarz, which predicts that the relaxation time of the dispersion is approximately given by

$$\tau = R^2/2ukT, \tag{12}$$

where R and u are the radius of a particle and the counterion mobility, respectively [8]. The relaxation times calculated by the use of eq. (12) are $\approx 4 \times 10^{-7}$ s for B-2 latex and 3×10^{-6} s for T-1 latex, assuming that the u-value of the H^+ ion in water at 25°C is $\approx 2.4 \times 10^9$ cgs units. The order of these evaluated values agrees with the observed values of the relaxation time at lower frequency. Schwarz has also predicted the magnitude of the dielectric increment as

$$\Delta\epsilon_l = \tfrac{9}{4}\phi\left(1+\tfrac{1}{2}\phi\right)^{-2} e_0^2 R\sigma_0/\epsilon_v kT, \tag{13}$$

where σ_0 is the charge density of the surface of a latex [7]. According to this theory, the magnitude of the dielectric increment at lower frequencies is ≈ 140 for B-2 latex at $\phi = 0.154$, which is very close to the observed ones. From these facts we can conclude that the dielectric dispersion at low frequency is induced by the polarization of the counterion on the surface of the spherical macroion as proposed by Schwarz.

Now, the dielectric increment at high frequency cannot be identified with the Maxwell–Wagner effect as described in the previous section. The observed dielectric increment at high frequency is much larger than that calculated from the Maxwell–Wagner equation,

$$\begin{aligned}\Delta\epsilon_h = {} & \left\{9(\epsilon_m\kappa_p - \epsilon_p\kappa_m)^2\phi(1-\phi)\right\}/ \\ & \times\left\{\left[2\epsilon_m+\epsilon_p+\phi(\epsilon_m-\epsilon_p)\right]\right. \\ & \left.\times\left[2\kappa_m+\kappa_p+\phi(\kappa_m-\kappa_p)\right]^2\right\}.\end{aligned} \tag{14}$$

The value of the increment estimated from eq. (14) is $\approx 5 \times 10^{-3}$ which cannot be observed by the present apparatus. Instead of eq. (14), Ballario et al. proposed an extended Maxwell–Wagner equation for the dielectric increment at high frequency in the case $\epsilon_p \ll \epsilon_m$, such that

$$\begin{aligned}\Delta\epsilon_h = {} & \left\{9\left[\epsilon_m(2/R)(\lambda+\lambda_0)\right]^2\phi(1-\phi)\right\}/ \\ & \left\{\epsilon_m(2+\phi)\left[\kappa_m(2+\phi)\right.\right. \\ & \left.\left.+(2/R)(\lambda+\lambda_0)(1-\phi)\right]^2\right\}\end{aligned} \tag{15}$$

where λ_0 and λ are the surface conductivities of a sphere at the high- and low-frequency limits, respectively. This equation has been derived by combining the Maxwell–Wagner and the Schwarz equations; the derivation is performed by the replacement of ϵ_p and κ_p in eq. (14) as follows:

$$\epsilon_p \to \epsilon_p + \frac{2\lambda_0\tau}{R(1+\omega^2\tau^2)},$$

$$\kappa_p \to \kappa_p + \frac{2\lambda}{R}\cdot\frac{2\omega^2\tau^2\lambda_0}{R(1+\omega^2\tau^2)}.$$

The evaluated value of $\Delta\epsilon_h$ from eq. (15) is, however, ≈ 0.2 for B-2 latex at $\phi = 0.154$ on the assumption that $\lambda + \lambda_0 \approx 10^{-9}\ \Omega^{-1}$. This fact indicates that eq. (15) is not relevant for the explanation of our present results. This is thought to be due to the neglect of the counterion distribution around the spherical macroion in the theoretical treatment of Ballario et al. [11].

The addition of acid enriches the net counterion density in the vicinity of a macroion surface. As seen in the previous section, the acid enlarges the magnitude of the increment at lower frequencies and depresses that at higher frequencies. Enhancement of the former is ascribed to the increase in the tangential component of the displacement current, which is consistent with the Schwarz theory. The addition of the acid, however, provides coions in the free space, leading to a depression of the ionic atmosphere around a macroion. This effect also reduces the radial component of the displacement current. Qualitatively, the dielectric increment at low frequencies and that at high frequencies are considered to be due to the tangential and radial components of the displacement current, respectively. Thus, the dispersions at low frequencies and at high frequencies are closely correlated with each other through the counterion distribution around a macroion. The diffused layer of counterions is considered to play an important role in the polarization mechanism of the latex suspension.

Theoretically, the multiconcentric layer model has been successful in interpreting the data on dielectrics in spherical biological systems [21–23]. In the present case, this diffused layer may have the form of a multiconcentric layer. A description of this situation by a new theoretical treatment will be given in a forthcoming paper.

When two species of counterions having different mobilities are mixed, the dispersion at low frequencies becomes broader whereas that of high frequencies remains unchanged. Also the average relaxation times of both dispersions increase as H^+ is replaced by Na^+. These results are interpreted in terms of the change in the average mobility of bound ions and its distribution. Namely, as shown in table 6, an increase in the average relaxation time with increasing Na^+ is in agreement with a decrease in the average mobility which may be obtained by the weighted average of the mobilities of H^+ and Na^+. The broadness of the dispersion at low frequencies is considered to be due to the distribution of the average counterion velocity in the vicinity of a single latex, that is, due to the heterogeneity in the composition of the bound counterions in each latex. For the dispersion at high frequencies, however, the reason why the dispersion pattern is unchanged seems to be so simple. In free space where the radial current occurs, the above mentioned heterogeneity in the composition is hardly expected, resulting in a narrow distribution of the relaxation times at high frequencies. Although the above mentioned reason is plausible, the true mechanism should be investigated more carefully in the future.

Acknowledgement

We wish to express our sincere thanks to Drs. N. Imai and A. Minakata for valuable discussions.

References

[1] I. Jungner, Acta Physiol. Scand. Suppl. 10 (1945) 32.
[2] I. Jungner and L.G. Allgén, Nature 163 (1949) 849.
[3] I. Jungner, Acta Physiol. Scand. Suppl. 20 (1950) 69.
[4] L.G. Allgén, Acta Physiol. Scand. Suppl. 22 (1950) 76.
[5] S. Takashima and A. Minakata, Digest of literature on dielectrics, Vol. 37, ed. W.E. Vaughan (National Academy of Sciences, Washington, DC, 1975), pp. 602–653.
[6] N. Imai and S. Sasaki, Biophys. Chem. 11 (1980) 361.
[7] H.P. Schwan, G. Schwarz, J. Maczuk and H. Pauly, J. Phys. Chem. 66 (1962) 2626.
[8] G Schwarz, J. Phys. Chem. 66 (1962) 2636.
[9] J.M. Schurr, J. Phys. Chem. 68 (1964) 2407.
[10] I.M. Williams and A.M. James, J. Chem. Soc. Faraday I 72 (1976) 803.
[11] C. Ballario, A. Bonincontro and C. Cametti, J. Colloid Interface Sci. 54 (1976) 415; 63 (1978) 567; 72 (1979) 304.
[12] K.W. Wagner, Arch. Elektrotech. 2 (1914) 371.
[13] P.A. Hiltner and I.M. Krieger, J. Phys. Chem. 73 (1969) 2386.
[14] H.P. Schwan, in: Physical techniques in biological research, Vol. 6B, ed. W.L. Nastuk (Academic Press, New York, 1963) Ch. 6.
[15] J.F. Johnson and R.H. Cole, J. Am. Chem. Soc. 73 (1951) 4536.
[16] W. Scheider, J. Phys. Chem. 79 (1975) 127.
[17] K.S. Cole and R.H. Cole, J. Chem. Phys. 9 (1941) 341.
[18] J.B. Rosen, J. Soc. Ind. Appl. Math. 8 (1960) 181.
[19] D. Goldfarb, SIAM. J. Appl. Math. 17 (1969) 739.
[20] O. Wiener, A.K.S.G. Wiss. Math. Phys. Kl. 32 (1912) 509.
[21] A. Irimajiri, Y. Doida, T. Hanai and A. Inouye, J. Membr. Biol. 28 (1978) 209.
[22] A. Irimajiri, T. Hanai and A. Inouye, J. Theor. Biol. 78 (1979) 251.
[23] T. Hanai, A. Ishikawa and N. Koizumi, Bull. Inst. Chem. Res. Kyoto Univ. 55 (1977) 376.