

A Study of Kinetics of Polystyrene Aggregation Progress Using Dynamic Light Scattering

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On the basis of dynamic light scattering, the kinetics of the aggregation process in salt-induced water solutions of polystyrene latex particles is investigated for various ionic strength ($0.1 \leq \mu \leq 2.5$). Our results show that aggregation of clusters can take place either slowly or rapidly, depending on the ionic strength. The rapid process can produce clusters with the fractal dimensions $d = 1.79 \pm 0.02$ for $2.0 \leq \mu \leq 2.5$ and $d = 1.75 \pm 0.02$ or 2.09 ± 0.05 for $0.4 \leq \mu \leq 1.5$. Clusters with $d = 1.75$ are always observed to restructure so as to yield $d = 2.09 \pm 0.05$. The slow process yields clusters for $0.1 \leq \mu \leq 0.15$. It is also shown that the results when electrolytes such as KCl, $MgCl_2$, and $CaCl_2$ are used as flocculating agent are the same as those for NaCl.

I. INTRODUCTION

In the past decade, many studies of the kinetics of the irreversible aggregation process have been made [1-13] in considerable detail for gold, silica, polystyrene, and protein colloids from both the experimental and the theoretical points of views in order to understand this type of nonequilibrium phenomena in terms of the properties of the scale invariance of the resulting clusters. The clusters are usually characterized by their fractal dimension d that relates the total mass M of the aggregate to its typical size R , i.e., $M \sim R^d$.

It is well-known from the theoretical point of view that, for irreversible aggregation in which clusters can not be separated into constituent monomers after sticking together, two regions of aggregation, characterized as diffusion-limited cluster-cluster aggregation (DLCA) and reaction-limited cluster-cluster aggregation (RLCA), appear in terms of the apparent rate-limiting step in the process [14]. In the former case, individual particles or clusters stick with a high probability upon contact and yield clusters with the fractal dimension $d = 1.75 \pm 0.05$. This rapid DLCA process is found to exhibit power-law kinetics with $R \sim t^{1/d}$, where R is the hydrodynamic radius of the clusters and t is the time [15,16]. On the other hand, in the slow RLCA process, the particles or clusters have a low sticking probability and produce clusters with the fractal dimension $d = 2.05 \pm 0.05$. The RLCA process exhibits exponential kinetics with $R \sim e^{\alpha t}$, where α depends on the experimental conditions [17,18].

Aggregation processes for various colloids have been investigated by means of many experimental techniques including computer simulation, X-ray scattering, neutron scattering, and light scattering [1-10]. Among these, light scattering has provided a powerful tool for characterizing the kinetics of aggregation because measurements of the scattered intensity and of the linewidth in a quasielastic experiment give information on the fractal dimension and the hydrodynamic radius of the cluster [19-24]. A series of very interesting measurements using the dynamic light-scattering technique have been recently performed on different colloids under various experimental conditions. Aubert and Cannell [25] have suggested that, for colloidal silica spheres, the radius of the clusters increases as $R \sim t^{1/d}$, where the slow process always yields clusters with the fractal dimension $d = 2.08 \pm 0.05$ and the rapid process produces clusters with either $d = 1.75 \pm 0.05$ or 2.08 ± 0.05 . In this case, clusters with $d = 1.75$ are always observed to restructure so as to yield $d = 2.08 \pm 0.05$. Bolle et al.'s experimental results [8] for polystyrene particles in a NaCl solution, however, show that clusters grow with $R \sim t^{1/d}$ with only $d = 1.75 \pm 0.03$ in the fast process and that restructuring of clusters with $d = 1.75$ to clusters with $d = 2.1$ does not take place. Furthermore, the largest cluster tends to precipitate before restructuring. Thus, we can see that the above two sets of experimental results are different from each other. It is, therefore, desirable to analyze the kinetics of the aggregation process of relatively large, but still Brownian, particles.

In this paper, we report a detailed investigation by means of dynamic light scattering of the kinetics of the aggregation process both for polystyrene latex particles induced by a salt (NaCl) under various ionic strengths and for polystyrene particles induced by salts such as KCl, MgCl₂, and CaCl₂ at a fixed ionic strength. Our results will be compared with other experimental and theoretical results.

II. EXPERIMENT

1. Dynamic Light-Scattering Measurements

In a homodyne dynamic light-scattering experiment, the normalized autocorrelation function $C(\tau)$ is related to the normalized scattered-field autocorrelation function $g(\tau)$ as [26]

$$C(\tau) = A + B |g(\tau)|^2 \quad (1)$$

where A and B are constants, and τ denotes the delay time. For monodispersed colloid particles, $g(\tau)$ is given by

$$g(\tau) = \exp(-Dq^2\tau) \quad (2)$$

Here, $q = (4\pi n/\lambda) \sin(\theta/2)$ denotes the scattering vector, with λ being the wavelength of the light, n the refractive index of the solution, θ the scattering angle, and D the translational diffusion coefficient. For a polydispersed system, the normalized autocorrelation function can be analyzed by the cumulants [26,27]. In general, the cumulant expansion is expressed as

$$C(\tau) = A + B \exp(-2K_1\tau + \frac{2K_2}{2!}\tau^2 - \frac{2K_3}{3!}\tau^3 + \dots) \quad (3)$$

where K_n denotes the n -th cumulant of $C(\tau)$. The first three cumulants are obtained from a third-order polynomial least-squares fit of the logarithm of the normalized autocorrelation function given by

$$\ln(C(\tau) - A) = \ln B - 2(K_1\tau - \frac{K_2}{2!}\tau^2 + \frac{K_3}{3!}\tau^3 + \dots) \quad (4)$$

and the first cumulant $K_1 (= Dq^2)$ is used to obtain the translational diffusion coefficient D , which can be related to the hydrodynamic radius R in terms of the Stokes-Einstein relationship; i.e., $D = kT/6\pi\eta R$ with k being the Boltzmann constant, T the absolute temperature, and η the viscosity of the solution. Thus, the hydrodynamic radius R can be calculated if K_1 (and hence D) is given by the dynamic light-scattering experiment.

In our experiment, we used a photon correlation spectroscopy apparatus that consisted of a BIC (Brookhaven Instruments Co.) BI-200SM goniometer and a BI-9000AT 232 channel correlator. In the goniometer, the incident radiation is supplied by a spectra-physics 10-mW He-Ne laser with a wavelength 6328 Å. The sample

holder is centered in a thermostated index-matching vat which is mounted on the pivot point of the optical rail holding the detector and which is filled with Decalin as an index-matching liquid. The scattering angle is selected by pivoting the rail around the index-matching vat. The scattered light is collected by an iris diaphragm and then focused by a 100-mm focal-length lens onto a selected pinhole (100, 200, 400 μm or 1, 2, 3 mm). The light that passes through the pinhole is focused by the detector optics onto a photomultiplier tube (PMT). The output of the PMT is sent to an amplifier-discriminator, and the resultant signal is sent to the Brookhaven BI-9000AT 232 channel correlator. The data obtained from the correlator are transferred to a computer for analysis. All measurements are done by using 12-mm cylindrical cuvettes at an angle of 90°. The temperature of the vat is kept $20 \pm 1^\circ\text{C}$ and room temperature was $21 \pm 1^\circ\text{C}$. The cumulant method [27] is used for data analysis to extract information on the average hydrodynamic size.

2. Sample Preparation

The polystyrene latex particles used in this research had radii of $R_0 = 0.057 \pm 0.01 \mu\text{m}$, and were purchased from the Sigma Chemical Co. as a suspension of 10%. The particles were filtered with a filter of pore size 0.45 μm in order to remove any dust. Before the measurement, they were diluted with triple-distilled deionized water to the desired concentration. The monomer concentration of the resulting solution was roughly 3×10^{11} ppls/cm³. A univalent-univalent electrolyte (NaCl) was used as a flocculating agent in the concentration range from 0.1 to 2.5 mol/l in order to study the kinetics of the aggregation process as a function of the ionic strength. Furthermore, to study the kinetics of the aggregation process for different salts at a fixed ionic strength, we used KCl, MgCl₂, and CaCl₂, instead of NaCl, as the flocculating agent. In this case, the ionic strength μ of solution is given by [28]

$$\mu = \sum_i (m_i Z_i^2) / 2 \quad (5)$$

where the m_i are the molar concentrations of the various ions in the solution and the Z_i are their charges.

III. RESULTS AND ANALYSIS

To test our BIC dynamic light-scattering apparatus, the intensity of the scattered light from only the index-matching liquid (Decalin) was measured at different angles. The percentage errors for the average of $I \sin \theta$ are presented in Fig. 1. We can see from Fig. 1 that the percentage errors of the alignment test for our apparatus are the same within 1% errors, except for the scattering angles of 15° and 155°. At an angle of 90°, the average

sphere diameter obtained from the BI-9000AT correlator was $0.108 \pm 0.02 \mu\text{m}$, which is in very good agreement with the manufacturer's specification ($0.114 \pm 0.02 \mu\text{m}$).

Figure 2(a) shows the growth of clusters with time for an ionic strength $\mu = 2.5$ corresponding to a salt (NaCl) concentration $c = 2.5 \text{ mol/l}$, where the solid square marks denote the experimental data and the solid line represents the linear least-squares fit for $R \sim t^{1/d}$ with $d = 1.80 \pm 0.03$, which agrees with diffusion-limited aggregation ($d = 1.75$) within the errors. The growth of clusters with time for an ionic strength $\mu = 1.5$ is

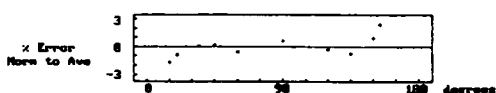


Fig. 1. The percentage errors for the average of $I \sin \theta$

shown in Fig. 2(b), where the solid and the dotted lines represent the linear least-squares fit for $R \sim t^{1/d}$ with $d = 1.75 \pm 0.03$ and $d = 2.08 \pm 0.02$, respectively. The transition time (T_t), which deviates from the linear least-squares fit with $d = 1.75$, is 150 min. The kinetics of the aggregation process were measured repeatedly while decreasing the ionic strength gradually. Figure 2(c) shows the growth of clusters for an ionic strength $\mu = 0.4$. The clusters form as $R \sim t^{1/d}$ with $d = 1.79 \pm 0.03$ (solid line) or 2.17 ± 0.02 (dotted line), which are similar to the results for $\mu = 1.5$. However, the transition time is 70 min which is much shorter than the 150 min for $\mu = 1.5$. As can be seen from Figs. 2(b) and 2(c), restructuring of clusters with $d = 1.75$ to clusters with $d = 2.1$ is observed for an ionic strength ranging from 0.4 to 1.5. In the case of $\mu = 0.3$, the radius of the clusters grows as $R \sim t^{1/d}$ with only $d = 2.08 \pm 0.03$, and restructuring of the clusters with $d = 1.75$ to clusters with $d = 2.1$ does

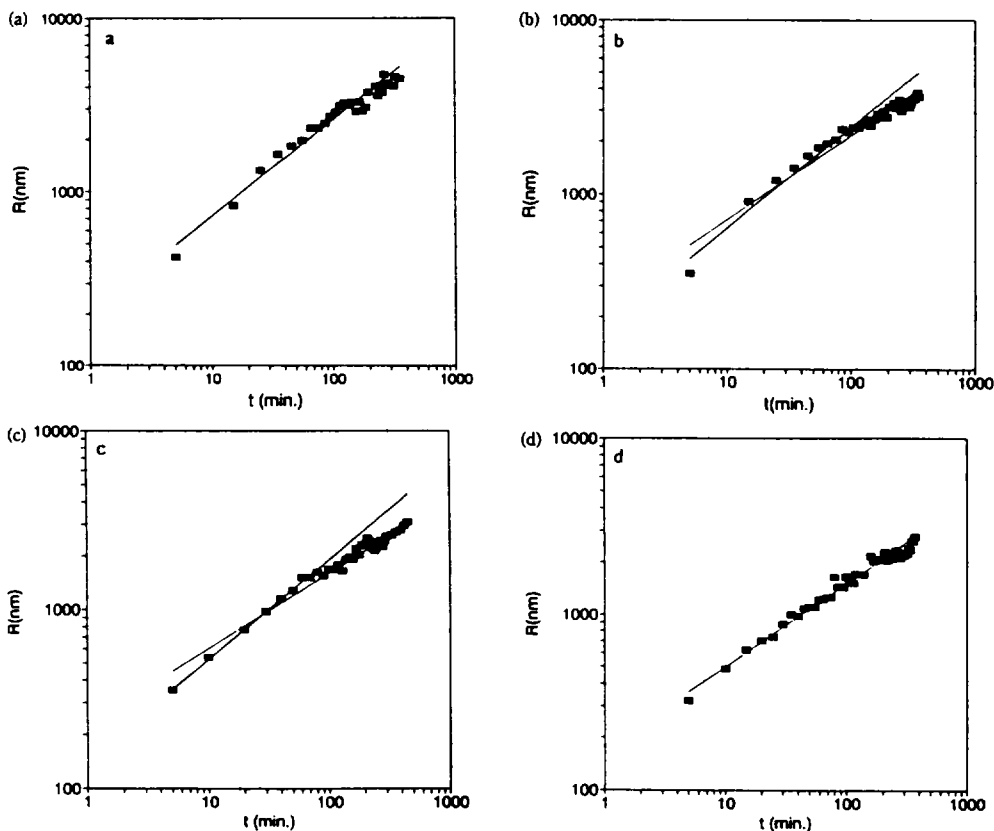


Fig. 2. Growth of clusters with time (a) for $\mu = 2.5$, where the solid line represents the linear least-squares fit of $R \sim t^{1/d}$ with $d = 1.80 \pm 0.03$, (b) for $\mu = 1.5$, where the solid and the dotted lines are for $R \sim t^{1/d}$ with $d = 1.75 \pm 0.03$ and $d = 2.08 \pm 0.02$, respectively, (c) for $\mu = 0.4$, where the solid and the dotted lines are for $R \sim t^{1/d}$ with $d = 1.79 \pm 0.03$ and $d = 2.17 \pm 0.02$, respectively, and (d) for $\mu = 0.3$, where the dotted line is for $R \sim t^{1/d}$ with $d = 2.08 \pm 0.03$.

not occur, as shown in Fig. 2(d).

Our results for an ionic strength $0.3 \leq \mu \leq 2.5$ are presented in Table 1 and Fig. 3. For an ionic strength $2.0 \leq \mu \leq 2.5$, the kinetic process of growth takes place rapidly, and the radius of the clusters grows as $R \sim t^{1/d}$ with only $d = 1.79 \pm 0.02$, which agrees with DLCA. For an ionic strength $0.4 \leq \mu \leq 1.5$, restructuring of the clusters with $d = 1.75 \pm 0.02$ to clusters with $d = 2.09 \pm 0.05$ takes place as discussed above. In this case, the clusters with $d = 1.75$ are always observed to restructure so as to yield clusters with $d = 2.09 \pm 0.05$. It is interesting to note that the aggregates with $d = 1.75$ or 2.09 are not stable and apparently restructure over periods of hours or more as the salt concentration is diluted. At the late stage of DLCA, we expect that the change of the aggregates with $d = 1.75$ to those with $d = 2.09$ takes place due to a change in the stick probability of the particles or the clusters. For $\mu = 0.3$, the aggregates form slowly with only $d = 2.08 \pm 0.03$ and have a more condensed structure. As seen from Table 1 and Fig. 3, as the ionic strength increases, the transition time of the fractal dimension from $d = 1.75$ to 2.1 gets longer little by little from 70 min for $\mu = 0.4$ to 150 min for $\mu = 1.5$. These results agree with those of Aubert and Cannell [25], but they are contrary to those of Bolle et al. [8], indicating that the largest clusters tend to precipitate before restructuring.

Figures 4 and 5 show the growth of clusters with time

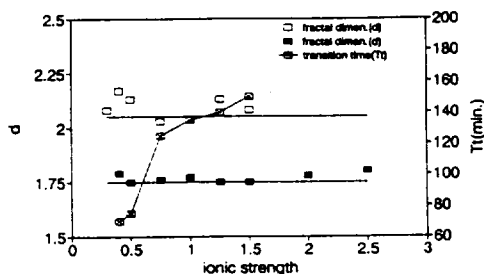


Fig. 3. The fractal dimension (d) and the transition time (T_i) as a function of the ionic strength (μ).

for the ionic strengths $\mu = 0.15$ and 0.1 , respectively. The clusters form as $R \sim e^{\alpha t}$, which agrees with RLCA, where α is 0.015 for $\mu = 1.5$ and 0.003 for $\mu = 1$. As shown in Figs. 4 and 5, little change in the radius of the clusters is observed after 200 min for $\mu = 0.15$ and after 900 min for

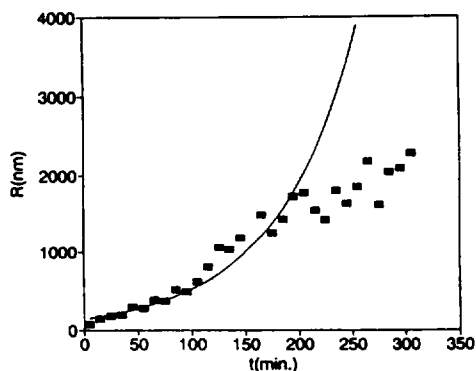


Fig. 4. Growth of clusters with time for $\mu = 0.15$. The solid line indicates the fit of $R \sim e^{\alpha t}$ with $\alpha = 0.03$.

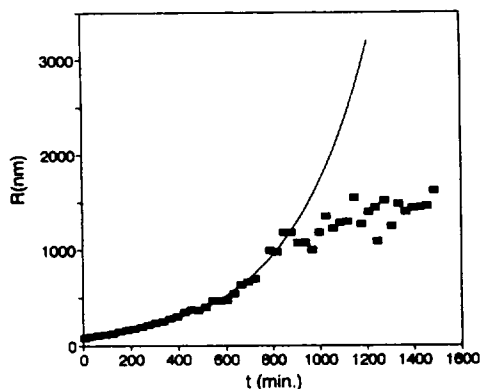


Fig. 5. Growth of clusters with time for $\mu = 0.1$. The solid line is for $R \sim e^{\alpha t}$ with $\alpha = 0.015$.

Table 1. The fractal dimension (d), the transition time (T_i) from $d = 1.75$ to 2.1 , and the time (t_R) to grow to $R = 1000$ nm for various ionic strengths (μ).

c (mol/l)	μ	d	T_i (min.)	t_R (min.)
0.3	0.3	2.08 ± 0.03	-	42
0.4	0.4	1.79 ± 0.02 (2.17 ± 0.02)	70	32
0.5	0.5	1.75 ± 0.02 (2.13 ± 0.02)	75	19
0.75	0.75	1.77 ± 0.04 (2.03 ± 0.03)	125	21
1	1	1.76 ± 0.02 (2.04 ± 0.02)	135	22
1.25	1.25	1.75 ± 0.03 (2.13 ± 0.03)	140	29
1.5	1.5	1.75 ± 0.03 (2.08 ± 0.02)	150	22
2	2	1.78 ± 0.02	-	22
2.5	2.5	1.80 ± 0.03	-	20

$\mu = 0.1$. The average radii of the clusters after these times are 1820 ± 400 nm for $\mu = 0.15$ and 1320 ± 170 nm for $\mu = 0.1$. It is very difficult to explain these phenomena theoretically and experimentally. These mechanisms of these phenomena are unclear at this moment.

The time for growing to a cluster with a radius of 1000 nm is shown in Fig. 6 as a function of the ionic strength. This growing time tends to get shorter as the ionic strength increases because the repulsive force of particles surrounded with positive ions becomes weak as the ionic strength increases. As a result, the aggregates grow rapidly up to $R = 1000$ nm. However, for an

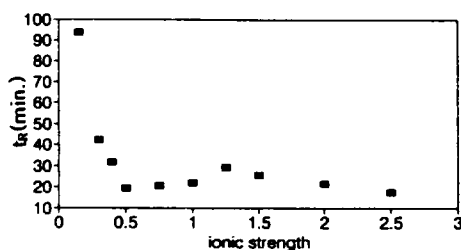


Fig. 6. The time (t_R) for growing to a cluster with a radius of 1000 nm as a function of the ionic strength (μ).

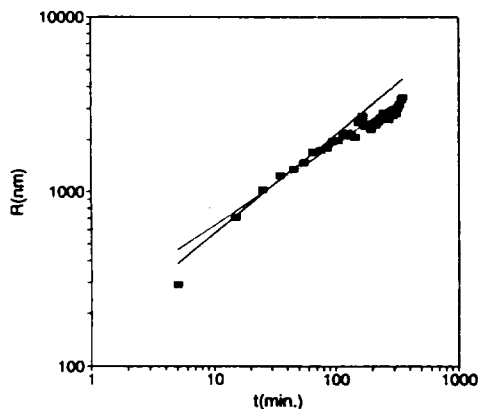


Fig. 7. Growth of clusters with time for KCl at an ionic strength $\mu = 1.5$. The solid and the dotted lines represent the linear least-squares fit of $R \sim t^{1/d}$ with $d = 1.76 \pm 0.03$ and $d = 2.07 \pm 0.02$, respectively.

ionic strength $1 \leq \mu \leq 2.5$, the average time required for $R = 1000$ nm is 23 ± 4 min, which does not depend on the ionic strength.

On the other hand, our results for different salts

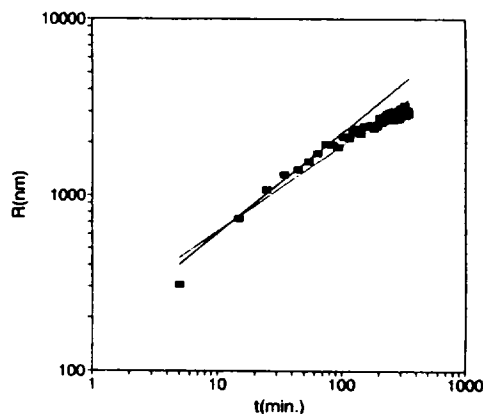


Fig. 8. Growth of clusters with time for MgCl_2 at $\mu = 1.5$. The solid and the dotted lines represent the linear least-squares fit of $R \sim t^{1/d}$ with $d = 1.75 \pm 0.03$ and $d = 2.05 \pm 0.02$, respectively.

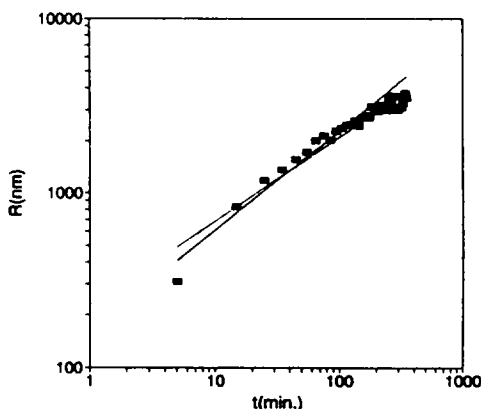


Fig. 9. Growth of clusters with time for CaCl_2 at $\mu = 1.5$. The solid and the dotted lines represent the linear least-squares fit of $R \sim t^{1/d}$ with $d = 1.75 \pm 0.02$ and $d = 2.05 \pm 0.02$, respectively.

Table 2. The fractal dimension (d), the transition time (T_t) from $d = 1.75$ to 2.1 , and the time (t_R) to grow to $R = 1000$ nm for different salts with an identical ionic strength (μ).

salt	c (mol/l)	μ	d	T_t (min.)	t_R (min.)
NaCl	1.5	1.5	1.75 ± 0.03 (2.08 ± 0.02)	150	22
KCl	1.5	1.5	1.76 ± 0.03 (2.07 ± 0.02)	140	29
MgCl_2	0.5	1.5	1.75 ± 0.03 (2.05 ± 0.02)	170	24
CaCl_2	0.5	1.5	1.75 ± 0.02 (2.05 ± 0.02)	140	28

(KCl, MgCl₂, and CaCl₂) having the identical ionic strength $\mu = 1.5$, which is induced in water solutions of polystyrene, are presented in Figs. 7, 8, and 9 and in Table 2. To fix the ionic strength at $\mu = 1.5$, the salt concentrations should be $c = 1.5 \text{ mol/l}$ for the univalent-univalent electrolyte KCl and $c = 0.5 \text{ mol/l}$ for the bivalent-univalent electrolytes MgCl₂ and CaCl₂, respectively. The kinetic process of growth follows $R \sim t^{1/d}$ with $d = 1.74 \pm 0.02$ or 2.06 ± 0.02 ; hence, the restructuring of the aggregates takes place for these electrolytes, which coincides with the result for NaCl at an ionic strength $\mu = 1.5$. The average time required for $R = 1000 \text{ nm}$ is $25 \pm 3 \text{ min}$, which does not depend on the kind of salt. Thus, we can see that the kinetic process of the aggregates does not depend on the salt concentration or the kind of salt, but relies on the ionic strength of the solution.

IV. CONCLUSIONS

In this paper we have investigated the kinetics of aggregation process in the salt induced water solutions of polystyrene latex particles using the dynamic light scattering, where the appropriate amount of a univalent-univalent electrolyte (NaCl, KCl) or a bivalent-univalent electrolyte (MgCl₂, CaCl₂) were used as flocculating agent. For ionic strength $2.0 \leq \mu \leq 2.5$ with high salt concentration, the kinetic process of growth takes place rapidly and the clusters form with $R \sim t^{1/d}$ with only $d = 1.79 \pm 0.02$, which agrees with DLCA, while for $0.4 \leq \mu \leq 1.5$, the restructuring of clusters with $d = 1.75 \pm 0.02$ to 2.09 ± 0.05 takes place. In this case, clusters with $d = 1.75$ are always observed to restructure so as to yield $d = 2.09 \pm 0.05$. It is interesting to note that the aggregates with $d = 1.75$ or 2.09 are not stable and apparently restructure over periods of hours or more as the salt concentration is diluted. However, for $\mu = 0.3$ with low salt concentration, the aggregates form slowly with only $d = 2.08 \pm 0.03$ and have more condensed structure. In the case that the salt concentration is more diluted, i.e., $0.1 \leq \mu \leq 0.15$, the radius of cluster grows with $R \sim e^{\alpha t}$, which agrees with RLCA during a certain time. Furthermore, it is also shown that, at a fixed ionic strength of $\mu = 1.5$, results of electrolytes such as KCl, MgCl₂, and CaCl₂ used as flocculating agent are identical with those of NaCl. Thus, we can conclude that the kinetic process of the aggregates does not depend on concentration or kind of electrolytes but rely on the ionic strength of solutions.

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